Supporting information

Synthesis of Tri- and Disubstituted Fluorenols and Derivatives Thereof by Using Catalytic [2+2+2] Cyclotrimerization

Ilaria Caivano, Reinhard Kaiser, Florian Schnurrer, Jiří Mosinger, Ivana Císařová, David Nečas and Martin Kotora*

Contents

I General

Where possible, reagents were purchased form commercial sources (Sigma-Aldrich, Acros Organics, Fluorochem and Strem Chemicals companies.) Solvents were purified and dried by distillation: tetrahydrofuran (THF) from sodium/benzophenone, dichloromethane from calcium hydride. Other solvents and all reagents were used without further purification. All reactions were performed under argon atmosphere unless otherwise noted. Chromatography was performed on Merck Silica gel 60 from Sigma-Aldrich. Thin layer chromatography was performed on Merck silica gel 60 F_{254} coated aluminum sheets. The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker AVANCE III Spectrometer (^{1}H at 600 MHz and ^{13}C at 151 MHz), Bruker AVANCE III HD Spectrometer (^{1}H at 400 MHz, ^{13}C at 101 MHz and ^{19}F at 376.5 MHz) or Varian NMR Solutions 300 (^{1}H at 300 MHz and ^{13}C at 75 MHz) as solutions in $CDCl_3$, CD_2Cl_2, acetone-d_6 or $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Chemical shifts are given in δ-scale. ^{1}H NMR spectra were referenced to residual peak of $CDCl_3$ (^{1}H, δ = 7.26; ^{13}C, δ = 77.0), CD_2Cl_2 (^{1}H, δ = 5.32; ^{13}C, δ = 53.5) and acetone-d_6 (^{1}H, δ = 2.05; ^{13}C, δ = 29.8), coupling constants J are given in Hz. The IR spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer in KBr powder and are reported in wave numbers (cm^{-1}). The MS spectra were recorded on an Agilent 5975 Inert MSD or GC×GC-TOFMS LECO Pegasus IVD device. The UV/Vis absorption spectra were recorded using Unicam 340 spectrometer. Microwave reactions were performed in a Biotage Initiator device.

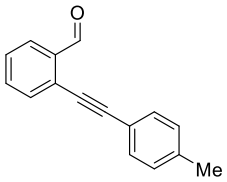
Crystallographic data were collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube at 150 K. Corrected steady-state emission spectra were recorded on an Aminco Bowman (AB2) spectrometer. The absolute quantum yields were recorded on Quantaurus-QY Plus UV-NIR absolute PL quantum yield spectrometer (Hamamatsu). All melting points are uncorrected and were determined on a melting point apparatus KB T3000 (the temperature range room temperature–260 ℃).

II Synthesis of starting material

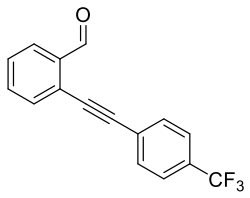
A_1: General procedure for Sonogashira reaction.[1] To a solution of triethylamine (0.30 M) and THF (0.30 M) in a Schlenk flask were added 2-bromobenzaldehyde (6.0 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (0.3 mmol, 5 mol%) and CuI (0.6 mmol, 10 mol%) under argon. Then the terminal alkyne **2** (7.2 mmol, 1.2 eq.) was added and the resulting mixture was stirred for 3 h under reflux. After being cooled down, the reaction mixture was filtered through a pad of Celite®/silica gel, washed with diethyl ether, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products.

A_2: General procedure for Sonogashira and desilylation reaction.[2] 1-Iodio-4-nitrobenzene (5.0 mmol, 1.0 eq.) was dissolved in triethylamine (0.36 M) and stirred for 10 min. under argon. Then CuI (0.28 mmol, 5.5 mol%), $Pd_2(dba)_3$ (0.14 mmol, 2.8 mol%) and PPh_3 (0.28 mmol, 5.5 mol%) were added. After addition of trimethylsilylacetylene **2h** the reaction was stirred for 4 h at 20 °C. The reaction mixture was concentrated under reduced pressure and used for the next step without purification. To a solution of the crude in MeOH (10 mL), MeOH/KOH (10 mL, 1 M) was added dropwise and the resulting mixture was stirred for 15 min. After removal of methanol, the reaction mixture was extracted with diethyl ether (3 × 30 mL), the combined organic layers were washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products.

2-(*p*-Tolylethynyl)benzaldehyde (S-1a). With 2-bromobenzaldehyde (584 µL, 5.0 mmol) and 1-ethynyl-4-methylbenzene **2b** (763 µL, 6.0 mmol) following the general procedure A_1. Column chromatography (10/1 hexanes/EtOAc) yielded 975 mg (89%) of the title compound as pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.42 (m, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 139.4, 135.7, 133.7, 133.1, 131.6, 129.3, 128.4, 127.17, 127.15, 119.2, 96.6, 84.3, 21.6. The spectral data were in accordance with previously published results.[3]



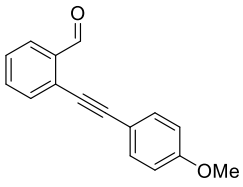
2-((4-(Trifluoromethyl)phenyl)ethynyl)benzaldehyde (S-1b). With 2-bromobenzaldehyde (817 µL, 7.0 mmol) and 1-ethynyl-4-(trifluoromethyl)benzene **2e** (1.37 mL, 8.4 mmol) following the general procedure A_1. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 1.76 g (92%) of the title compound as a yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.97 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.58–7.71 (m, 6H), 7.50 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 136.0, 133.8, 133.4, 131.9, 130.7 (q, $^2J_{C\text{-}F}$ =



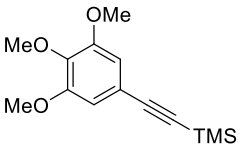
[1] D. Peña, D. Pérez, E. Guitián, L. Castedo; *Eur. J. Org. Chem.* **2003**, 1238-1243.
[2] T-D. Nguyen, V.-S. Dang, V.-H. Nguyen, T. M.-T. Nguyen, C.-H. Dang; *Polycyclic Aromatic Compounds.* **2018**, *38*, 42-50.
[3] M. Alfonsi, M. Dell´Acqua, D. Facoetti, A. Arcadi, G. Abbiati, E. Rossi; *Eur. J. Org. Chem.* **2009**, 2852-2862.

32.8 Hz), 129.2, 123.8 (q, $^{1}J_{C\text{-}F}$ = 272.3 Hz), 127.6, 126.1, 125.8, 125.5 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 94.5, 87.2; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.90. The spectral data were in agreement with the previously published results.[4]

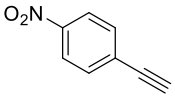
2-((4-Methoxyphenyl)ethynyl)benzaldehyde (S-1c). With 2-bromobenzaldehyde (715 µL, 6.0 mmol) and 1-ethynyl-4-methoxybenzene **2a** (963 µL, 7.2 mmol) following the general procedure A_1. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 1.34 g (94%) of the title compound as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (d, *J* = 0.7 Hz, 1H), 7.94 (ddd, *J* = 7.6, 1.2, 0.5 Hz, 1H), 7.59–7.63 (m, 1H), 7.57 (dt, *J* = 7.6, 1.7 Hz, 1H), 7.51 (dt, *J* = 9.0, 2.7 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 6.91 (dt, *J* = 9.0, 2.7 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 160.2, 135.6, 134.0, 133.7, 133.2, 133.0, 128.2, 127.3, 127.2, 114.4, 114.2, 96.6, 83.8, 55.3. The spectral data were in agreement with the previously published results.[5]



Trimethyl((3,4,5-trimethoxyphenyl)ethynyl)silane (S-2a). With 5-bromo-1,2,3-trimethoxybenzene (1.02 g, 4.1 mmol) and trimethylsilylacetylene **2h** (699 µL, 4.9 mmol)following the general procedure A_1. Column chromatography on silica gel (7/1 hexanes/EtOAc) gave 498 mg (46%) of the title compound as a pale brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (s, 2H), 3.76 (s, 9H), 0.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 138.8, 117.8, 108.9, 104.9, 92.7, 60.6, 55.8, -0.3; The spectral data were in agreement with the previously published results.[6]



1-ethynyl-4-nitrobenzene (S-2b). With 1-iodo-4-nitrobenzene (1.24 g, 5.0 mmol) and trimethylsilylacetylene **2h** (1.10 mL, 7.5 mmol) following the general procedure A_2. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 576 mg (78%) of the title compound as a pale brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 3.36 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 132.9, 128.8, 123.5, 82.3, 81.5; The spectral data were in agreement with the previously published results.[7]



[4] Chen, J.; Liu, B.; Chen, Y.; He, Q.; Yang, Q. *RSC Adv.* **2014**, *4*, 11168-11175.

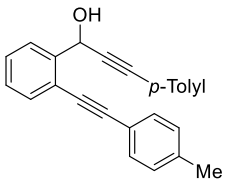
[5] Obika, S.; Kono, H.; Yasui, Y.; Yanada, R.; Takemoto, Y.; *J. Org. Chem.* **2007**, *72*, 4462-4468.

[6] Agabekov, V; Seiche, W; Breit, B; *Chem. Sci*., **2013**, *4*, 2418-2422.

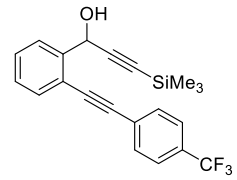
[7] Serwinski, P., R.; Lahti, P., M.; *Org. Lett*., **2003**, *5*, 2099-2102.

B: General procedure for alkynylation reaction[1] (preparation of 1). To a solution of terminal alkyne **2** (7.9 mmol, 1.4 eq.) in anhydrous THF (0.42 M), *n*-BuLi (1.6 M in hexane, 7.9 mmol, 1.4 eq.) was added dropwise at -78 ℃. After stirring for 30 min at -78 ℃, compound an aldehyde (5.7 mmol, 1.0 eq.) in THF (0.88 M) was added. The resulting mixture was stirred for 5 min at -78 ℃ and gradually warmed to 20 ℃. Once the starting materials have disappeared (TLC monitoring, typically 3h), the mixture was quenched with the saturated aqueous NH_4Cl solution. The aqueous layer was extracted with diethyl ether (3 × 30 mL), the combined organic layers were washed with the saturated solution of $NaHCO_3$, dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue on silica gel provided products.

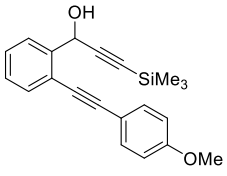
3-(*p*-Tolyl)-1-(2-(*p*-tolylethynyl)phenyl)prop-2-yn-1-ol (1c). With **S-1a** (975 mg, 4.4 mmol) and 1-ethynyl-4-methylbenzene **2b** (837 µL, 6.6 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 1.1 g (96%) of the title compound as pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.26 (m, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.04 (d, *J* = 5.1 Hz, 1H), 2.84 (d, *J* = 5.9 Hz, 1H), 2.24 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 138.8, 138.6, 132.4, 131.7, 131.5, 129.2, 129.0, 128.7, 128.2, 126.8, 121.7, 119.7, 119.4, 95.3, 87.6, 86.7, 86.0, 63.9, 21.52, 21.45. The spectral data were in accordance with previously published results.[8]



1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S-3a). With **S-1b** (949 mg, 3.5 mmol) and trimethylsilylacetylene **2h** (680 µL, 4.8 mmol) following the general procedure B. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 1.15 g (89%) of the title compound as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.64 (m, 4H), 7.57 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.43 (td, *J* = 7.6, 1.5 Hz, 1H), 7.35 (td, *J* = 7.6, 1.2 Hz, 1H), 5.92 (d, *J* = 5.9 Hz, 1H), 2.56 (br. s, 1H), 0.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 132.5, 131.7, 130.1 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.3, 128.2, 126.6, 123.8 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 125.2 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 120.8, 104.4, 93.3, 91.5, 88.9, 63.4, -0.3; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.77; IR (KBr) ν_{max} 3058, 3028, 2956, 2926, 2881, 2854, 2217, 1598, 1488, 1473, 1461, 1443, 1251, 1186, 1111, 1075, 842, 776, 752 692 cm^{-1}; HRMS (EI) *m/z* for $C_{21}H_{19}O_3Si$ $(M)^+$ calcd: 372.1157, found: 372.1155; R_f (5/1 hexanes/EtOAc) = 0.56.



1-(2-((4-methoxyphenyl)ethynyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S-3b). With **S-1c** (1.30 g, 5.7 mmol) and trimethylsilylacetylene **2h** (1.1 mL, 7.9 mmol) following the general procedure B. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 1.76 g (93%) of the title compound as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.45 - 7.57 (m, 3H), 7.37 (td, *J* = 7.7, 1.6 Hz, 1H), 7.31 (td, *J* = 7.6, 1.5 Hz,



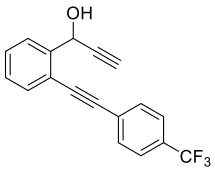
[8] J. Lian, R. Liu; *Chem. Comm.* **2007**, 1337-1339.

1H), 6.89 (d, *J* = 9.0 Hz, 2H), 5.94 (d, *J* = 4.4 Hz, 1H), 3.82 (s, 3H), 2.82 (br. s., 1H), 0.19 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 141.7, 133.0, 132.1, 128.4, 128.2, 126.7, 121.9, 114.8, 114.0, 104.4, 95.1, 91.3, 85.3, 63.7, 55.3, -0.2. The spectral data were in agreement with the previously published results. [9]

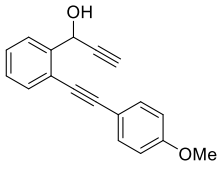
[9] Samanta, D.; Cinar, M. E.; Das, K.; Schmittel, M.; *J. Org. Chem.* **2013**, *78,* 1451−1462

C: General Procedure for desilylation reaction (preparation of 5). The starting trimethylsilated alkyne (5.25 mmol, 1.0 eq.) was dissolved in MeOH (0.23 M) with catalytic amount of H_2O. Subsequently, the resulting mixture was cooled down to 0 ℃ followed by addition of K_2CO_3 (10.5 mmol, 2.0 eq.). The reaction was carried out for 3h at the same low temperature. The mixture was neutralized with HCl (2 M) and extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using hexanes/EtOAc as eluent.

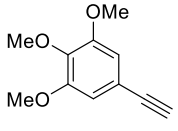
1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)prop-2-yn-1-ol (5a). With **S-3a** (2.34 g, 5.9 mmol) following the general procedure C. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 1.65 g (93%) of the title compound as an orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.59 (m, 5H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 5.97 (br. s., 1H), 3.28 (br. s., 1H), 2.67 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 132.5, 131.7, 130.1 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 129.4, 128.3, 126.5, 125.2 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 123.8 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 120.6, 93.4, 88.7, 82.9, 74.7, 62.9; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.79; IR (KBr) ν_{max} 3295, 3061, 3024, 2955, 2924, 2855, 1593, 1489, 1471, 1446, 1391, 1250, 1102, 1069, 1000, 848, 755 cm^{-1}; HRMS (CI) *m/z* for $C_{18}H_{12}OF_3$ $(M+H)^+$ calcd: 301.0840, found: 301.0839; R_f (5/1 hexanes/EtOAc) = 0.35.



1-(2-((4-methoxyphenyl)ethynyl)phenyl)prop-2-yn-1-ol (5b). With **S-3b** (1.80 g, 5.2 mmol) following the general procedure C. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 1.20 g (90%) of the title compound as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.54 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.35 (td, *J* = 7.6, 1.5 Hz, 1H), 7.30 (td, *J* = 7.3, 1.5 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.99 (br. s., 1H), 3.77 (s, 3H), 3.40 (br. s., 1H), 2.67 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 141.3, 132.8, 131.9, 128.4, 128.1, 126.3, 121.4, 114.6, 113.9, 94.9, 85.1, 83.1, 74.4, 62.6, 55.1; IR (KBr) ν_{max} 3476, 3446, 3387, 3366, 3297, 3288, 3067, 3013, 2932, 2836, 2214, 1607, 1565, 1509, 1461, 1446, 1290, 1248, 1180, 1153, 1111, 1093, 1030, 952, 839, 812, 761, 671, 641 cm^{-1}; HRMS (CI) *m/z* for $C_{18}H_{15}O_2$ $(M+H)^+$ calcd: 263.1072, found: 263.1071; R_f (5/1 hexanes/EtOAc) = 0.26.



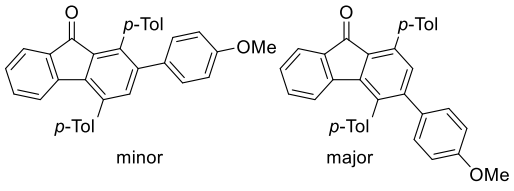
5-ethynyl-1,2,3-trimethoxybenzene (S-4). With **S-2a** (477 mg, 1.8 mmol) following the general procedure C. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 319 mg (88%) of the title compound as a pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 2H), 3.84 (s, 3H), 3.84 (s, 6H), 3.02 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 139.2, 117.0, 109.3, 83.6, 76.2, 60.9, 56.1. The spectral data were in agreement with the previously published results.[5]



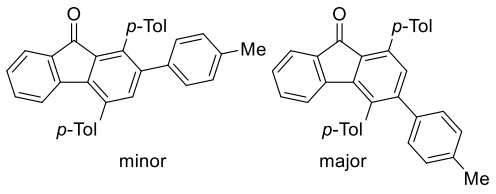
III Cyclotrimerization reactions and oxidation for 4

D: General procedure for cyclotrimerization with Wilkinson's catalyst $RhCl(PPh_3)_3$ and subsequent oxidation. (Preparation of 4). A dry microwave vial was charged with the starting material **1c** (0.25 mmol, 1.0 eq.), a terminal alkyne **2** (0.50 mmol, 2.0 eq.) and dissolved under argon atmosphere in THF (0.017 M). After addition of Wilkinson's catalyst (0.0075 mmol, 7 mg, 3 mol%) and the additive Ag_2CO_3 (0.015 mmol, 4 mg, 6 mol%) the reaction mixture was sealed and heated up to 180 °C for 1.5 h in a microwave reactor. The reaction mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. The residue was dissolved in anhydrous CH_2Cl_2 and pyridinium chlorochromate (PCC) (0.375 mmol, 81 mg, 1.5 eq.) and Celite® (64 mg) was added. The resulted mixture was stirred for 3 h at 25 °C. Afterwards the residue was filtered through a Celite®/silica gel plug. Column chromatography of the residue on silica gel yielded products.

2-(4-Methoxyphenyl)-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4a) and 3-(4-methoxyphenyl)-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4'a). With **1c** (80 mg, 0.25 mmol) and 1-ethynyl-4-methoxybenzene **2a** (64 µL, 0.5 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 50 mg (43%) the title compounds as an inseparable mixture (**4a**:**4'a** = 1:3.2) as a light yellow solid: mp (decomp) 155-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.50-7.55 (m, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.30-7.36 (m, 3H), 7.14 - 7.19 (m, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.82 (m, 1H), 6.70 (d, *J* = 8.6 Hz, 2H), 3.75 (s, 3H), 2.48 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 158.4, 143.4, 142.5, 140.5, 139.3, 138.1, 137.9, 137.2, 136.7, 136.6, 134.9, 134.0, 133.1, 132.3, 131.5, 130.8, 129.9, 129.4, 128.8, 128.4, 128.3, 123.8, 122.9, 113.2, 55.1, 21.40, 21.36; IR (KBr) ν_{max} 3018, 2949, 2922, 2828, 1712, 1667, 1612, 1508, 1463, 1436, 1405, 1287, 1249, 1201, 1177, 1104, 1083, 1059, 1038, 1018, 997, 938, 890, 831, 759 cm^{-1}; HRMS (ESI) *m/z* for $C_{34}H_{26}O_2Na$ $(M+Na)^+$ calcd: 489.18250, found: 489.18241; R_f (5/1 hexanes/EtOAc) = 0.35.

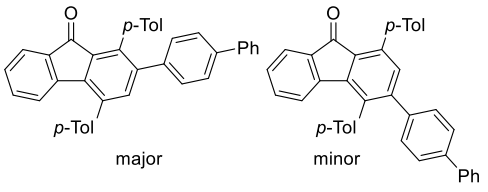


1,2,4-Tris(*p*-tolyl)-9*H*-fluoren-9-one (4b) and 1,3,4-tris(*p*-tolyl)-9*H*-fluoren-9-one (4'b). With **1c** (80 mg, 0.25 mmol) and 1-ethynyl-4-methylbenzene **2b** (64 µL, 0.5 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 35 mg (31%) the title compounds as an inseparable mixture (**4b**:**4'b** = 1:1.6) as a bright yellow solid: mp 209-214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.60 (d, *J* = 6.8 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.28 (s, 1H), 7.17 - 7.19 (m, 2H), 7.12 (d, *J* = 6.6 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.05 (m, 1H), 6.99 - 7.01 (m, 3H), 6.25 (d, *J* = 7.6 Hz, 1H), 2.46 (s, 3H), 2.44 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (major and minor) 193.0, 192.8, 148.0, 143.9, 143.6, 143.4, 142.8, 141.0, 140.6, 139.3, 138.2, 138.0, 137.9, 137.22, 137.18, 136.9, 136.7, 136.5, 136.3, 135.6, 135.1, 134.9, 134.6, 133.98, 133.95, 133.3, 133.0, 131.5, 129.9, 129.5, 129.4, 129.33, 129.31, 129.1, 128.8, 128.6, 128.5,

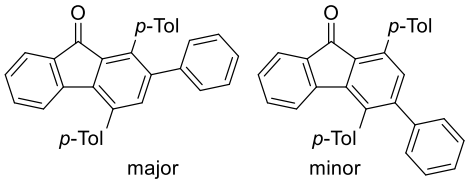


128.45, 128.38, 128.2, 123.8, 123.6, 123.3, 122.9, 21.39, 21.37, 21.35, 21.12, 21.09; IR (KBr) ν_{max} 3024, 2922, 2865, 1906, 1710, 1602, 1549, 1514, 1464, 1378, 1356, 1309, 1277, 1199, 1183, 1160, 1112, 1086, 1073, 1020, 952, 935, 905, 891, 860, 825, 814, 779, 757, 742, 724, 709, 656, 623, 557, 532, 501, 471 cm^{-1}; HRMS (ESI) *m/z* for $C_{34}H_{27}O$ $(M+H)^+$ calcd: 451.20564, found: 451.20571; R_f (10/1 hexanes/EtOAc) = 0.48.

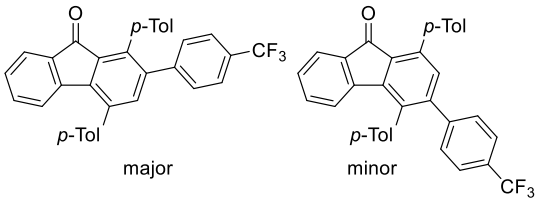
2-([1,1'-Biphenyl]-4-yl)-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4c) and 3-([1,1'-biphenyl]-4-yl)-1,4- bis(*p*-tolyl)-9*H*-fluoren-9-one (4'c). With **1c** (80 mg, 0.25 mmol) and 4-ethynyl-1,1'-biphenyl **2c** (89 mg, 0.5 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 54 mg (42%) the title compounds as an inseparable mixture (**4c**:**4'c** = 1:0.7) as a bright yellow solid: mp (decomp) 170-175 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.51-7.54 (m, 4H), 7.41-7.39 (m, 6H), 7.29 (m, 3H), 7.23-7.19 (m, 4H), 7.10 (s, *J* = 7.8 Hz, 4H), 6.87 (m, 1H), 2.49 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (major and minor) 192.9, 147.6, 143.8, 143.7, 143.4, 142.4, 141.1, 140.9, 140.5, 140.4, 139.6, 139.4, 139.3, 139.2, 139.0, 138.15, 138.06, 138.0, 137.4, 137.3, 136.9, 136.5, 135.6, 135.1, 134.9, 134.8, 134.5, 134.0, 133.2, 133.1, 132.9, 131.6, 130.1, 130.0, 129.9, 129.5, 129.4, 129.1, 129.0, 128.8, 128.73, 128.71, 128.63, 128.57, 128.5, 128.3, 127.35, 127.26, 126.9, 126.4, 126.3, 123.8, 123.6, 123.4, 123.0, 21.40, 21.37; IR (KBr) ν_{max} 3024, 2916, 2863, 1915, 1704, 1622, 1603, 1584, 1548, 1510, 1469, 1403, 1364, 1309, 1275, 1235, 1183, 1161, 1109, 1085, 1040, 1021, 1007, 971, 937, 892, 844, 824, 807, 764, 727, 697, 604, 544, 500, 480 cm^{-1}; HRMS (ESI) *m/z* for $C_{39}H_{29}O$ $(M+H)^+$ calcd: 513.22129, found: 513.22162; R_f (10/1 hexanes/EtOAc) = 0.39.



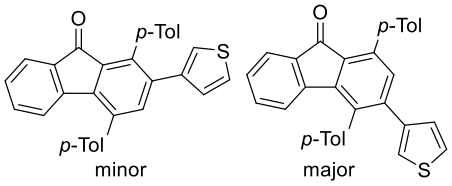
2-Phenyl-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4d) and 3-phenyl-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4'd). With **1c** (80 mg, 0.25 mmol) and phenylacetylene **2d** (55 μL, 0.5 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 25 mg (23%) the title compounds as an inseparable mixture (**4d**:**4'd** = 1:0.8) as a bright yellow solid: mp (decomp) 207-212 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.50 - 7.56 (m, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.37 (s, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.15 - 7.20 (m, 5H), 7.01 - 7.12 (m, 6H), 6.80 - 6.87 (m, 1H), 2.49 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 143.4, 142.9, 140.8, 139.9, 139.4, 138.2, 137.9, 137.2, 136.8, 136.5, 134.9, 134.0, 132.9, 131.5, 129.9, 129.7, 129.4, 128.8, 128.5, 128.2, 127.7, 126.7, 123.8, 123.0, 21.37, 21.36; IR (KBr) ν_{max} 3052, 3024, 2921, 2860, 1911, 1711, 1670, 1602, 1555, 1517, 1464, 1439, 1380, 1308, 1279, 1183, 1157, 1112, 1086, 1074, 1021, 952, 937, 905, 823, 814, 769, 757, 702, 658, 616, 539, 500, 465 cm^{-1}; HRMS (ESI) *m/z* for $C_{33}H_{25}O$ $(M+H)^+$ calcd: 437.18999, found: 437.19003; R_f (10/1 hexanes/EtOAc) = 0.45.



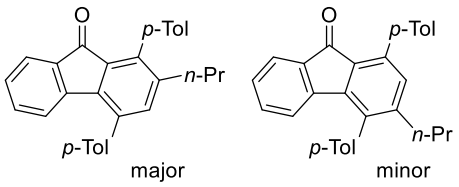
1,4-Bis(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (4e) and 1,4-bis(*p*-tolyl)-3-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (4'e). With **1c** (80 mg, 0.25 mmol) and 1-ethynyl-4-(trifluoromethyl)benzene **2e** (82 μL, 0.5 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 33 mg (26%) the title compounds as an inseparable mixture (**4e**:**4'e** = 1:1) as a bright yellow solid: mp (decomp) 224-229 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major and minor) δ 7.59 (d, *J* = 6.8 Hz, 1H), 7.52 - 7.56 (m, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.40 - 7.46 (m, 6H), 7.34 (m, 2H), 7.33 (s, 1H), 7.29 (s, 1H), 7.26 - 7.28 (m, 2H), 7.24 - 7.25 (m, 1H), 7.15 - 7.23 (m, 8H), 7.13 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 4H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.82 - 6.87 (m, 1H), 6.26 (d, *J* = 7.6 Hz, 1H), 2.49 (s, 3H), 2.44 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.71, 192.67, 146.4, 143.8, 143.6, 143.1, 141.6, 141.3, 141.2, 139.3, 138.3, 138.2, 138.0, 137.7, 137.4, 137.3, 136.2, 135.4, 135.0, 134.9, 134.24, 134.22, 134.16, 133.1, 132.4, 131.6, 130.0, 129.9, 129.8, 129.8, 129.5, 129.1, 128.84, 128.75, 128.5, 124.8, 124.7 (q, $^{3}J_{C-F}$ = 3.8 Hz), 124.6, 124.0, 123.8, 123.4, 123.2, 21.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.44, -62.49; IR (KBr) ν_{max} 3027, 2923, 2871, 1711, 1614, 1603, 1552, 1516, 1446, 1405, 1322, 1276, 1166, 1128, 1086, 1070, 1019, 950, 937, 848, 824, 811, 755, 727, 660, 625, 542, 481 cm^{-1}; HRMS (ESI) *m/z* for $C_{34}H_{24}F_3O$ $(M+H)^+$ calcd: 505.17738, found: 505.17746; R_f (10/1 hexanes/EtOAc) = 0.42.



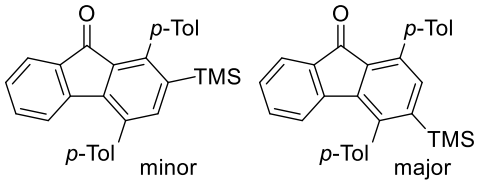
2-(Thien-3-yl)-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4f) and 3-(thien-3-yl)-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4'f). With **1c** (80 mg, 0.25 mmol) and 3-ethynyl-thiophene **2f** (49 μL, 0.5 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 20 mg (18%) the title compounds as an inseparable mixture (**4f**:**4'f** = 1:1.3) as a bright yellow solid: mp (decomp) 218-223 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.57 (d, *J* = 6.6 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.35 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 - 7.20 (m, 3H), 6.96 (dd, *J* = 2.9, 1.2 Hz, 1H), 6.22 (d, *J* = 7.3 Hz, 1H), 2.46 (s, 3H), 2.44 (s, 3H); ^{1}H NMR (400 MHz, $CDCl_3$) (minor) δ 7.51 - 7.53 (m, 1H), 7.33 (s, 1H), 7.16 - 7.18 (m, 4H), 7.08 - 7.13 (m, 6H), 6.92 (dd, *J* = 2.9, 1.2 Hz, 1H), 6.82 - 6.86 (m, 2H), 6.73 (dd, *J* = 5.1, 1.2 Hz, 1H), 2.49 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (major and minor) 192.9, 192.7, 143.8, 143.7, 143.4, 142.3, 141.1, 140.4, 140.2, 139.1, 138.1, 138.0, 137.7, 137.4, 137.37, 137.26, 137.1, 136.4, 135.23, 135.21, 135.1, 134.8, 134.5, 134.04, 134.97, 133.4, 132.6, 131.7, 129.6, 129.6, 129.5, 129.1, 128.8, 128.6, 128.54, 128.50, 124.5, 124.4, 123.8, 123.7, 123.6, 123.4, 123.0, 21.5, 21.4; IR (KBr) ν_{max} 3025, 2920, 2873, 1709, 1603, 1552, 1515, 1464, 1414, 1305, 1277, 1185, 1112, 1087, 1021, 966, 908, 864, 824, 812, 791, 781, 757, 736, 709, 667, 542, 480 cm^{-1}; HRMS (ESI) *m/z* for $C_{31}H_{22}SONa$ $(M+Na)^+$ calcd: 465.12836, found: 465.12843; R_f (10/1 hexanes/EtOAc) = 0.42.



2-Propyl-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4g) and 3-propyl-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4'g). With **1c** (80 mg, 0.25 mmol) and 1-pentyne **2g** (49 μL, 0.5 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 25 mg (25%) the title compounds as an inseparable mixture (**4g**:**4'g** = 1:0.7) as a bright yellow solid: mp (decomp) 158-163 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.53 (d, *J* = 6.8 Hz, 1H), 7.47-7.49 (m, 2H), 7.32-7.35 (m, 2H), 7.27-7.29 (m, 2H), 7.21-7.22 (m, 2H), 7.20 (s, 1H), 7.10-7.15 (m, 2H), 6.04 (d, *J* = 7.6 Hz, 1H), 2.51 (s, 3H), 2.44 (s, 3H), 2.39-2.41 (m, 2H), 1.45-1.53 (m, 2H), 0.82-0.85 (m, 3H); ^{1}H NMR (400 MHz, $CDCl_3$) (minor) δ 7.39-7.41 (d, *J* = 7.6 Hz, 2H), 7.32-7.35 (m, 2H), 7.27-7.29 (m, 2H), 7.15-7.12 (m, 4H), 7.07 (t, *J* = 7.6 Hz, 2H), 6.78 (d, *J* = 6.8 Hz, 1H), 2.49 (s, 3H), 2.46 (s, 3H), 2.39-2.41 (m, 2H), 1.45-1.53 (m, 2H), 0.82-0.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) (major and minor) δ 192.9, 148.6, 143.9, 143.4, 142.7, 141.0, 137.8, 137.8, 137.6 , 136.9, 137.0, 136.5, 135.18, 135.15, 134.9, 133.9, 133.8, 131.8, 129.7, 129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 128.23, 128.17, 128.1, 127.7, 123.7, 123.5, 123.0, 122.7, 35.3, 34.2, 24.2, 24.1, 21.44, 21.38, 14.0, 13.9; IR (KBr) ν_{max} 3025, 2957, 2926, 2867, 1710, 1602, 1552, 1518, 1463, 1306, 1184, 1113, 1088, 1020, 989, 909, 822, 752, 536 cm^{-1}; HRMS (ESI) *m/z* for $C_{30}H_{27}O$ $(M+H)^+$ calcd: 403.20564, found: 403.20574; R_f (10/1 hexanes/EtOAc) = 0.51 (silica gel plate).



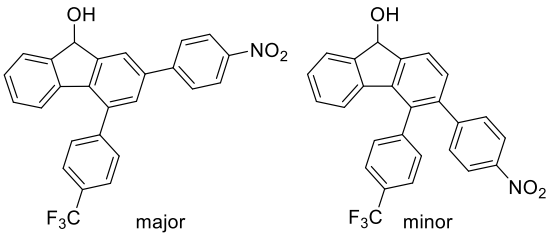
1,4-Bis(*p*-tolyl)-2-(trimethylsilyl)-9*H*-fluoren-9-one (4h) and 1,4-bis(*p*-tolyl)--3-(trimethylsilyl)-9*H*-fluoren-9-one (4'h). With **1c** (80 mg, 0.25 mmol) and ethynyltrimethylsilane **2h** (69 μL, 0.5 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 16 mg (15%) the title compounds as an inseparable mixture (**4h**:**4'h** = 1:2.4) as a bright yellow solid: mp (decomp) 141-146 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.51 (s, 1H), 7.40-7.42 (m, 3H), 7.33-7.35 (m, 2H), 7.24-7.26 (m, 3H), 7.15-7.18 (m, 3H), 6.79-6.81 (m, 1H), 2.50 (s, 3H), 2.46 (s, 3H), 0.01 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) (major and minor) δ 193.5, 148.3, 146.8, 144.4, 143.5, 142.7, 142.0, 141.8, 139.6, 137.9, 137.8, 137.2, 137.2, 137.0, 136.3, 136.2, 135.0, 134.8, 134.6, 134.0, 133.9, 130.5, 129.7, 129.4, 129.3, 129.1, 129.0, 128.8, 128.8, 128.6, 128.3, 128.2, 123.7, 123.3, 123.1, 21.5, 21.4, 0.54, 0.49; IR (KBr) ν_{max} 3039, 3022, 2953, 2918, 1709, 1602, 1553, 1515, 1460, 1267, 1242, 1222, 1177, 1025, 962, 880, 841, 817, 765 cm^{-1}; HRMS (ESI) *m/z* for $C_{30}H_{28}ONaSi$ $(M+Na)^+$ calcd: 455.18016, found: 455.18007; R_f (10/1 hexanes/EtOAc) = 0.58 (silica gel plate).



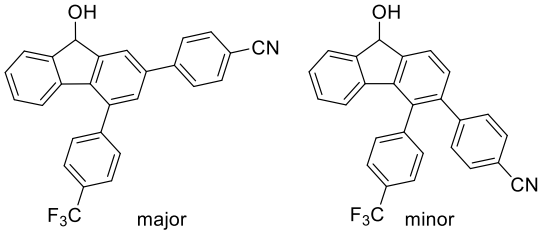
IV Cyclotrimerization reactions for 6

E: General procedure for cyclotrimerization with Cp*Ru(Cod)Cl (Preparation of 6). To a stirred solution of starting material **5a** (0.5 mmol, 150 mg, 1.0 eq.) in CH_2Cl_2 (0.083 M) and under argon atmosphere, the terminal alkyne **2** (1.0 mmol, 2.0 eq.) was added. Then Cp*Ru(cod)Cl (0.05 mmol, 19 mg, 10 mol%) was added and the reaction mixture was stirred for 4h at 25 ℃. After concentration under reduced pressure, silica gel column chromatography with hexanes/EtOAc as eluent was used for purification.

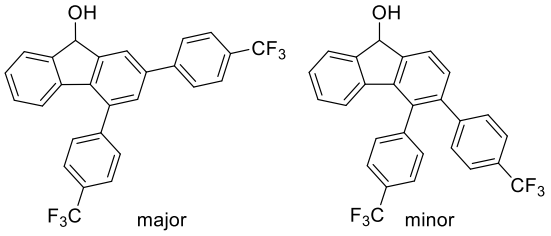
2-(4-Nitrophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6a). With **5a** (30.0 mg, 0.10 mmol) and 1-ethynyl-4-nitrobenzene **2** (29.4 mg, 0.20 mmol) following the general procedure E. Column chromatography on silica gel (2/1 hexanes/EtOAc) gave 13.7 mg (31%) of the title compound (the separated minor regioisomer compound was formed in the ratio of 3:1, determined by ^{1}H-NMR of the reaction mixture) as a yellow solid: mp (decomp) 210-212; ^{1}H NMR (400 MHz, $CDCl_3$) 8.32 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 0.7 Hz, 1H), 7.76 - 7.89 (m, 4H), 7.60 - 7.73 (m, 3H), 7.49 (d, *J* = 1.5 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.71 (s, 1H), 1.79 (br. s., 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 147.2, 146.6, 146.5, 143.7, 138.7, 138.0, 137.6, 136.9, 130.3 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 130.0, 129.4 (br.), 129.1, 128.4, 127.7, 125.8 (br.), 125.5 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 125.2, 124.2, 123.5, 122.9, 74.7; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.41; IR (KBr) ν_{max} 3500, 3089, 3084, 1598, 1518, 1455, 1344, 1326, 1174, 1117, 1105, 1072, 1027, 845, 833, 752, 743 cm^{-1}; HRMS (ESI) *m/z* for $C_{26}H_{15}O_3NF_3$ $(M\text{-}H)^-$ calcd: 446.10095, found: 446.10025; R_f (2/1 hexanes/EtOAc) = 0.30.



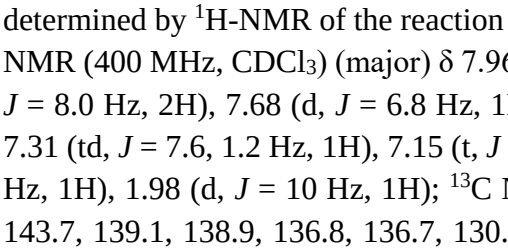
4-(9-Hydroxy-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-2-yl)benzonitrile (6b). With **5a** (150 mg, 0.50 mmol) and 4-ethynylbenzonitrile **2** (127 mg, 1.00 mmol) following the general procedure E. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 30 mg (14%) of the title compound (the separated minor regioisomer compound was formed in the ratio of 3:1, determined by ^{1}H-NMR of the reaction mixture) as a pale brown solid: mp (decomp) 246-253 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.95 (s, 1H), 7.73 - 7.83 (m, 6H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 1.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.70 (br. s., 1H), 1.97 (br. s., 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 146.4, 144.7, 143.8, 138.7, 138.4, 137.3, 136.8, 132.7, 130.4 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 129.8, 129.1, 128.3, 127.6, 127.4, 125.8 (br), 125.2, 124.2 (q, $^1J_{C\text{-}F}$ = 270.2 Hz), 123.4, 122.9, 118.8, 111.3, 74.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.41; ATR ν_{max} 3428, 3076, 2929, 2851, 2226, 1604, 1512, 1455, 1404, 1332, 1278, 1168, 1120, 1072, 1024, 899, 839, 752 cm^{-1}; HRMS (EI) *m/z* for $C_{27}H_{14}NOF_3$ $(M\text{-}2H)^+$ calcd: 425.1027, found: 425.1029; R_f (5/1 hexanes/EtOAc) = 0.18.



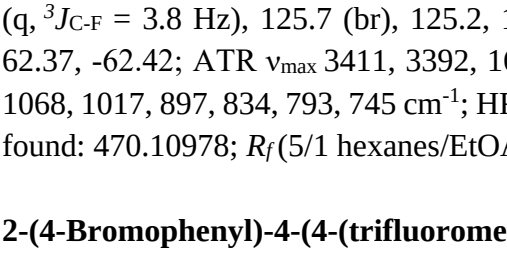
2,4-Bis(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6c). With **5a** (150 mg, 0.54 mmol) and 4-ethynyl-α,α,α-trifluorotoluene **2e** (175 µL, 1.07 mmol) following the general procedure E. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 89 mg (35%) of the title compound (the separated minor regioisomer compound was formed in the ratio of 5:1, determined by ^{1}H-NMR of the reaction mixture) as a brown solid: mp (decomp) 184-87 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.96 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.76 - 7.82 (m, 4H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 6.8 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 1.6 Hz, 1H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.15 (t, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.70 (d, *J* = 9.8 Hz, 1H), 1.98 (d, *J* = 10 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.4, 144.9, 143.9, 143.7, 139.1, 138.9, 136.8, 136.7, 130.4, 129.5, 129.4 (br), 129.9, 129.0, 128.2, 127.3, 125.9 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.7 (br), 125.2, 123.4, 122.8, 74.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.37, -62.42; ATR ν_{max} 3411, 3392, 1616, 1511, 1454, 1407, 1394, 1328, 1290, 1166, 1103, 1068, 1017, 897, 834, 793, 745 cm^{-1}; HRMS (APCI) *m/z* for $C_{27}H_{16}OF_6$ $(M)^+$ calcd: 470.10999, found: 470.10978; R_f (5/1 hexanes/EtOAc) = 0.23.



2-(4-Bromophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6d). With **5a** (162 mg, 0.54 mmol) and 1-bromo-4-ethynylbenzene **2** (196 mg, 1.08 mmol) following the general procedure E. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 83 mg (32%) of the title compound (the separated minor regioisomer compound was formed in the ratio of 4:1, determined by ^{1}H-NMR of the reaction mixture) as light brown solid: mp (decomp) 229-235 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.91 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.62-7.55 (m, 4H), 7.41 (d, *J* = 2 Hz, 1H), 7.29 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14 (td, *J* = 7.6, 0.8 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.68 (br, d, *J* = 10 Hz, 1H), 1.99 (br, d, *J* = 10.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.3, 144.08, 144.07, 139.4, 139.1, 139.0, 136.6, 136.3, 132.0, 130.0, 129.5 (br), 129.0, 128.6, 128.0, 125.7 (br), 125.5, 125.1, 123.1, 122.6, 122.0, 74.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.38; IR (KBr) ν_{max} 3434, 3387, 3043, 2926, 2860, 1494, 1455, 1401, 1323, 1290, 1180, 1126, 1072, 1033, 1009, 893, 851, 824, 752 cm^{-1}; HRMS (ESI) *m/z* for $C_{26}H_{15}OBrF_3$ $(M\text{-}H)^-$ calcd: 479.02639, found: 479.02618; R_f (3/1 hexanes/EtOAc) = 0.35.

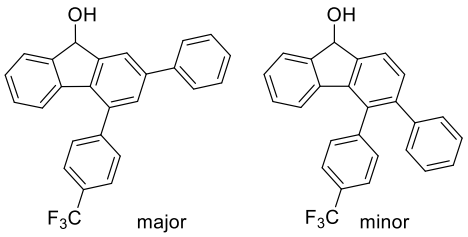


2-(Naphth-1-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6e). With **5a** (150 mg, 0.54 mmol) and 1-ethynylnaphthalene **2** (154 µL, 1.08 mmol) following the general procedure E. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 72 mg (29%) of the title compound (the separated minor regioisomer compound was formed in the ratio of 10:1, determined by ^{1}H-NMR of the reaction mixture) as a brown solid: mp (decomp) 189-192 ℃; ^{1}H NMR (400 MHz, $CDCl_3$)

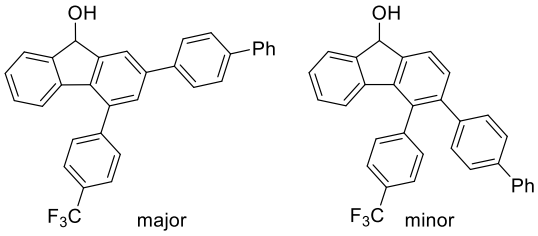


(major) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.86 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 6.8 Hz, 3H), 7.59-7.44 (m, 4H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.72 (br. s., 1H), 1.99 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 146.4, 144.1, 140.3, 139.2, 139.2, 136.1, 135.8, 133.8, 132.6, 131.4, 130.1 (q, $^{2}J_{C\text{-}F}$ = 32.1 Hz), 129.5 (br.), 128.9, 128.4, 128.0, 127.9, 127.1, 126.3, 126.3, 125.9, 125.7, 125.6 (br.), 125.4, 125.1, 122.6, 74.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.32; IR (KBr) ν_{max} 3338, 3050, 2920, 2860, 1926, 1619, 1575, 1508, 1464, 1448, 1391, 1318, 1160, 1119, 1106, 1068, 1040, 1014, 894, 843, 802, 780, 736 cm^{-1}; HRMS (MALDI) *m/z* for $C_{30}H_{19}F_3O$ $(M)^+$ calcd: 452.1388, found: 452.1383; R_f (5/1 hexanes/EtOAc) = 0.28.

2-Phenyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6f). With **5a** (151 mg, 0.50 mmol) and phenylacetylene **2d** (110 µL, 1.01 mmol) following the general procedure E. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 81 mg (40%) of the title compound (the separated minor regioisomer compound was formed in the ratio of 10:1, determined by ^{1}H-NMR of the reaction mixture) as a pale brown solid: mp (decomp) 189-195 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.95 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.68-7.63 (m, 5H), 7.46 (m, 3H), 7.38 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.28 (td, *J* = 7.4, 0.8 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.68 (br s, 1H), 2.00 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.4, 144.3, 140.6, 140.1, 139.1, 136.5, 135.8, 130.2, 129.9, 129.7 (br), 128.9, 128.8, 127.8, 127.7, 127.0, 125.6 (br), 125.1, 123.3, 122.9, 122.5, 74.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.34; ATR ν_{max} 3419, 3055, 3031, 2923, 1619, 1458, 1413, 1395, 1329, 1290, 1162, 1123, 1105, 1066, 1024, 893, 848, 764, 749, 698 cm^{-1}; HRMS (ESI) *m/z* for $C_{26}H_{16}OF_3$ $(M\text{-}H)^-$ calcd: 401.11587, found: 401.11554; R_f (3/1 hexanes/EtOAc) = 0.35.

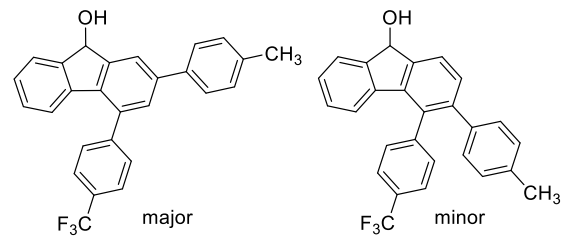


2-([1,1'-Biphenyl]-4-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6g). With **5a** (151 mg, 0.50 mmol) and 4-ethynylbiphenyl **2c** (183 mg, 1.01 mmol) following the general procedure E. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 98 mg (41%) of the title compound (the separated minor regioisomer compound was formed in the ratio of 7:1, determined by ^{1}H-NMR of the reaction mixture) as light brown solid: mp (decomp) 220-227 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 8.01 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.78 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.71 (dt, *J* = 8.4, 2.0 Hz, 2H), 7.68-7.66 (m, 5H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.48 (tt, *J* = 7.6, 2.0 Hz, 2H), 7.38 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.30 (td, *J* = 7.6, 0.8 Hz, 1H), 7.15 (td, J = 7.6, 0.4 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.72 (br d, *J* = 9.6 Hz, 1H), 1.98 (br d, *J* = 9.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 146.4, 144.3, 140.6, 140.5, 140.1, 139.1, 139.0, 136.9, 136.6, 135.9, 130.2, 129.6, 129.4 (br), 128.9, 128.8, 127.9, 127.6, 127.5, 127.4, 127.0, 125.6 (br), 125.1, 123.1, 122.6, 74.9; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.34; IR (KBr) ν_{max} 3423, 3043, 2917, 1606, 1455, 1404, 1332, 1272, 1174, 1126, 1108, 1066,

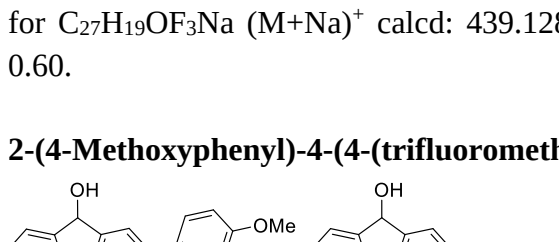


1027, 1003, 973, 923, 896, 836, 770, 740, 695 cm^{-1}; HRMS (ESI) *m/z* for $C_{32}H_{20}OF_3$ $(M-H)^-$ calcd: 477.14717, found: 477.14647; R_f (3/1 hexanes/EtOAc) = 0.34.

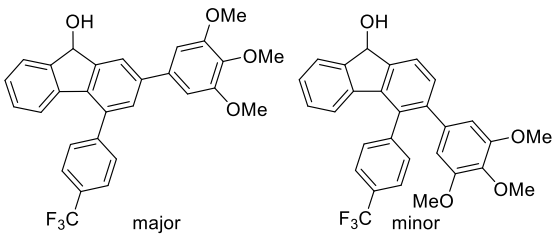
2-(*p*-Tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6h). With **5a** (74 mg, 0.24 mmol) and 4-ethynyltoluene **2b** (64 µL, 0.49 mmol) following the general procedure E. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 46.5 mg (46%) of the two inseparable title regioisomer compounds in the ratio of 10:1 as a pale brown solid: mp (decomp) 181-186 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.94 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.65 (m, 3H), 7.58 (dt, *J* = 8.0, 2.0 Hz 2H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.25-7.29 (m, 3H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.68 (d, *J* = 10 Hz, 1H), 2.41 (s, 3H), 1.94 (d, *J* = 10 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 146.3, 144.4, 140.6, 139.2, 137.6, 137.2, 136.5, 135.6, 130.1, 129.9, 129.6, 129.5, 129.3 (br), 128.9, 127.7, 126.9, 125.6 (br), 125.1, 123.1, 122.5, 74.9, 21.1; IR (KBr) ν_{max} 3482, 3048, 3052, 3028, 2972, 2850, 1604, 1457, 1324, 1251, 1220, 1160, 1122, 1104, 1066, 1014, 954, 846, 818, 741 cm^{-1}; HRMS (ESI) *m/z* for $C_{27}H_{19}OF_3Na$ $(M+Na)^+$ calcd: 439.12802, found: 439.12787; R_f (5/1 hexanes/EtOAc) = 0.60.



2-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6i). With **5a** (150 mg, 0.50 mmol) and 4-ethynylanisole **2a** (130 µL, 1.00 mmol) following the general procedure E. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 77 mg (36%) of the two inseparable title regioisomer compounds in the ratio of 10:1 as a pale brown solid: mp (decomp) 201-206 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.90 (d, *J* = 1.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.66-7.60 (m, 5H), 7.41 (d, *J* = 1.6 Hz, 1H), 7.26 (td, *J* = 7.6, 0.8, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 5.65 (br s, 1H), 3.86 (s, 3H), 2.02 (br s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 147.6, 146.3, 144.4, 140.3, 139.3, 136.5, 135.2, 132.6, 130.1 (q, $^2J_{C-F}$ = 32.1 Hz), 129.2, 128.9, 128.1, 127.7, 125.6 (br), 125.1, 125.0, 122.8, 122.5, 114.4, 113.2, 74.9, 55.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.34; IR (KBr) ν_{max} 3419, 3058, 2944, 2836, 1604, 1518, 1458, 1443, 1410, 1320, 1290, 1251, 1180, 1117, 1063, 1027, 890, 851, 830, 749 cm^{-1}; HRMS (EI) *m/z* for $C_{27}H_{17}O_2F_3$ $(M-2H)^+$ calcd: 430.1181, found: 430.1182; R_f (5/1 hexanes/EtOAc) = 0.25.

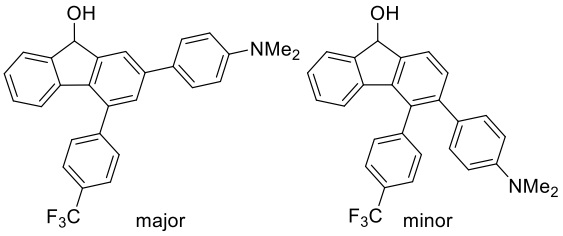


4-(4-(Trifluoromethyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-9*H*-fluoren-9-ol (6j). With **5a** (250 mg, 0.83 mmol) and 5-ethynyl-1,2,3-trimethoxybenzene **S-4** (320 mg, 1.66 mmol) following the general procedure E. Column chromatography on silica gel (5/1/1 DCM/hexanes/EtOAc) gave 222 mg (54%) of the two inseparable title regioisomer compounds in



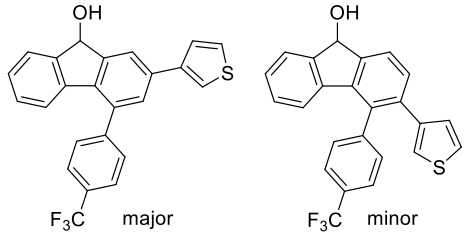
the ratio of 20:1 as a brown solid: mp (decomp) 101-103 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.91 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 3H), 7.40 (d, *J* = 1.5 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.78 - 6.89 (m, 3H), 5.68 (br. s, 1H), 3.94 (s, 6H), 3.90 (s, 3H), 2.13 (br. s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 147.6, 146.3, 144.2, 140.7, 139.1, 138.0, 136.4, 136.1, 135.9, 130.1 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.6 (br.), 129.5, 128.9, 127.8, 125.6 (br.), 125.1, 123.2, 122.5, 104.3, 74.8, 61.0, 56.3; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.33; IR (KBr) ν_{max} 3452, 2998, 2935, 2836, 1622, 1583, 1512, 1461, 1413, 1359, 1323, 1281, 1240, 1168, 1120, 1108, 1069, 1018, 1009, 964, 848, 830, 746 cm^{-1}; HRMS (ESI) *m/z* for $C_{29}H_{23}O_4F_3Na$ $(M+Na)^+$ calcd: 515.14406, found: 515.14364; R_f (5/1/1 DCM/hexanes/EtOAc) = 0.34.

2-(4-(*N*,*N*-Dimethylamino)phenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6k).



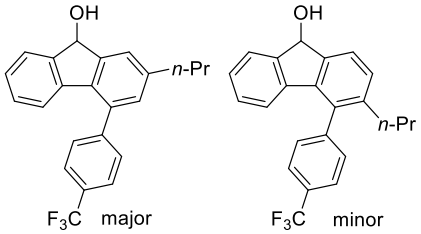
With **5a** (98 mg, 0.32 mmol) and 4-ethynyl-*N*,*N*-dimethylaniline (97 mg, 0.65 mmol) following the general procedure E. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 87 mg (60%) of the title compound (the separated minor regioisomer compound was formed in the ratio of 25:1, determined by ^{1}H-NMR of the reaction mixture) as a dark brown solid: mp (decomp) 104-106 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) 7.89 (s, 1H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.63 (m, *J* = 7.1 Hz, 3H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 1.7 Hz, 1H), 7.25 (td, *J* = 7.3, 0.7 Hz, 1H), 7.11 (t, *J* = 8.2 Hz, 1H), 6.78 - 6.88 (m, 3H), 5.63 (s, 1H), 3.00 (s, 6H), 2.17 (br. s., 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0 (br.), 147.6, 146.3, 144.6, 140.6, 139.4, 136.4, 134.5, 129.5 (br.), 129.5 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 128.7, 128.6, 127.6, 127.4, 125.5 (br.), 125.0, 124.2 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 122.3, 122.2, 113.0 (br.), 74.8, 40.7; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.28; IR (KBr) ν_{max} 3351, 3046, 2929, 2884, 2851, 2806, 1613, 1607, 1530, 1479, 1458, 1446, 1410, 1362, 1329, 1275, 1228, 1201, 1168, 1123, 1108, 1069, 1018, 955, 893, 851, 818, 740, 644, 606, 534, 510 cm^{-1}; HRMS (ESI) *m/z* for $C_{28}H_{23}ONF_3$ $(M+H)^+$ calcd: 446.17263, found: 446.17226; R_f (3/1 hexanes/EtOAc) = 0.30.

2-(Thien-3-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6l). With **5a** (130 mg, 0.43 mmol) and 3-ethynylthiophene **2f** (87 μL, 0.85 mmol) following the general procedure E. Column chromatography on silica gel (3/1 hexanes/ EtOAc) gave 107 mg (62%) of the two inseparable title regioisomer compounds in the ratio of 6:1 as a brown solid: mp (decomp) 177-183 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.94 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.66-7.62 (m, 3H), 7.55 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.47-7.45 (m, 2H), 7.42 (dd, *J* = 4.8, 2.8 Hz, 1H), 7.27 (td, *J* = 7.6, 0.8 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.66 (br s, 1H), 1.99 (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.3, 144.2, 141.4, 139.2, 136.5, 135.6, 135.3, 130.1 (q, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 129.6, 129.4 (br.), 128.9, 127.8, 126.6, 126.2, 125.6 (br.), 125.1, 124.7, 122.6, 122.5, 120.8, 74.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.35; IR (KBr) ν_{max} 3510, 3100, 2923, 2854,

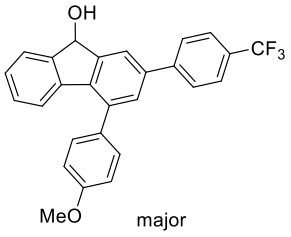


1458, 1404, 1326, 1171, 1123, 1105, 1069, 1036, 848, 785, 755 cm^{-1}; HRMS (ESI) *m/z* for $C_{24}H_{14}OF_3S$ $(M-H)^-$ calcd: 407.07229, found: 407.07196; R_f (3/1 hexanes/EtOAc) = 0.30.

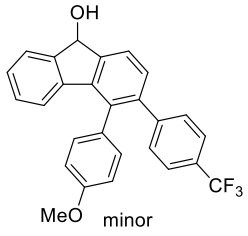
2-Propyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6m). With **5a** (192 mg, 0.64 mmol) and pent-1-yne **2g** (320 µL, 3.21 mmol) following the general procedure E. Column chromatography on silica gel (7/1 hexanes/EtOAc) gave 62 mg (26%) of the title compound (the separated minor regioisomer compound was formed in the ratio of 4:1, determined by ^{1}H-NMR of the reaction mixture) as a brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.56 - 7.65 (m, 3H), 7.53 (d, *J* = 0.7 Hz, 1H), 7.23 (td, *J* = 7.5, 1.0 Hz, 1H), 7.10 (td, *J* = 7.6, 0.7 Hz, 1H), 7.03 (d, *J* = 1.2 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.58 (d, *J* = 9.3 Hz, 1H), 2.68 (t, *J* = 7.3 Hz, 2H), 1.91 (d, *J* = 9.8 Hz, 1H), 1.72 (sxt, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 146.1, 144.5, 142.6, 139.5, 135.9, 134.3, 131.0, 129.9, 129.6, 129.3, 128.7, 127.4, 125.5 (br), 125.0, 124.8, 122.2, 74.8, 37.9, 24.5, 13.9; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.37; IR (KBr) ν_{max} 3461, 3303, 3049, 3028, 2962, 2932, 2869, 1619, 1458, 1401, 1380, 1329, 1248, 1222, 1168, 1129, 1105, 1069, 1024, 967, 952, 899, 881, 848, 797, 749, 632, 612 cm^{-1}; HRMS (ESI) *m/z* for $C_{23}H_{19}F_3NaO$ $(M+Na)^+$ calcd: 391.128137, found: 391.128021; R_f (7/1 hexanes/EtOAc) = 0.60.



4-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6n) and 4-(4-methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6n'). With **5b** (262 mg, 1.0 mmol) and 4-ethynyl-α,α,α-trifluorotoluene **2e** (336 µL, 2.00 mmol) following the general procedure E. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave the two separated title regioisomer compounds in the ratio of 4:1 as a brown solid:



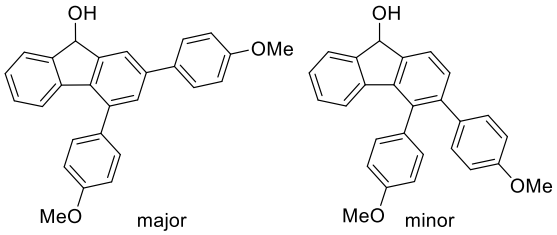
6n (major): 138 mg (32%); mp (decomp) 118-121 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 1.6 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.28 (td, *J* = 7.6, 0.8 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.64 (br. s, 1H), 3.93 (s, 3H), 2.31 (br. s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 147.6, 146.3, 144.0, 139.4, 138.7, 138.0, 137.1, 132.5, 130.2, 129.9 (br.), 129.4 (q, $^2J_{C-F}$ = 32.1 Hz), 128.8, 127.7, 127.2, 125.7 (q, $^3J_{C-F}$ = 3.8 Hz), 124.9, 124.2 (q, $^1J_{C-F}$ = 270.4 Hz), 123.0, 122.5, 114.0, 74.8, 55.3; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.34; IR (KBr) ν_{max} 3366, 3064, 2998, 2962, 2926, 2899, 2839, 1613, 1512, 1455, 1416, 1326, 1290, 1251, 1177, 1123, 1069, 1030, 1018, 955, 926, 896, 839, 749, 704, 662, 582 cm^{-1}; HRMS (ESI) *m/z* for $C_{27}H_{19}O_2F_3Na$ $(M+Na)^+$ calcd: 455.12294, found: 455.12259; R_f (3/1 hexanes/EtOAc) = 0.47.



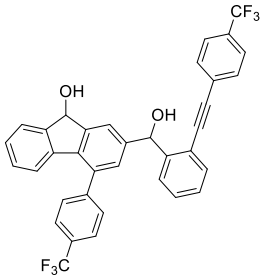
6n' (minor): 37 mg (8%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.20 - 7.25 (m, 3H), 7.14 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 1H), 7.00 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.89 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.84 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 5.65 (d, *J* = 9.5 Hz, 1H), 3.85 (s, 3H), 1.89 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (101

MHz, $CDCl_3$) δ 158.9, 146.3, 146.1, 144.9, 144.9, 141.6, 140.0, 138.6, 135.7, 131.3, 130.9, 130.5, 130.1, 129.3, 128.8, 128.4 (q, $^2J_{C-F}$ = 32.2 Hz), 127.6, 124.8, 124.2 (q, $^1J_{C-F}$ = 270.3 Hz), 124.1, 124.5 (q, $^3J_{C-F}$ = 3.8 Hz), 123.2, 114.0, 113.9, 74.6, 55.2; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.37; R_f (3/1 hexanes/EtOAc) = 0.37.

2,4-Bis(4-methoxyphenyl)-9*H*-fluoren-9-ol (6o). With **5b** (145 mg, 0.55 mmol) and 4-ethynylanisole **2a** (148 μL, 1.10 mmol) following the general procedure E. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 110 mg (51%) of the two inseparable title regioisomer compounds in the ratio of 7:1 as a brown solid: mp (decomp) 96-98 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.85 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.65-7.60 (m, 3H), 7.45 - 7.39 (m, 3H), 7.24 (td, *J* = 7.6, 1.2 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.64 (br. s., 1H), 3.92 (s, 3H), 3.86 (s, 3H), 1.96 (br. s., 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.25, 159.19, 147.4, 146.3, 140.0, 139.8, 137.8, 135.6, 133.0, 132.9, 130.8, 130.1, 129.5, 128.6, 128.0, 127.2, 124.8, 122.7, 121.9, 114.2, 113.9, 113.0, 74.9, 55.3; IR (KBr) ν_{max} 3411, 3384, 3070, 3046, 3028, 2995, 2953, 2932, 2902, 2836, 1610, 1512, 1455, 1437, 1329, 1290, 1245, 1183, 1117, 1030, 964, 943, 926, 896, 833, 788, 776, 749, 698, 650, 582, 534 cm^{-1}; HRMS (ESI) *m/z* for $C_{27}H_{22}O_3Na$ $(M+Na)^+$ calcd: 417.14612, found: 417.14633; R_f (3/1 hexanes/EtOAc) = 0.34.



2-(Hydroxy(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)methyl)-4-(4-(trifluoromethyl) phenyl)-9*H*-fluoren-9-ol (7). With **5a** (74 mg, 0.24 mmol) following the general procedure E. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 30 mg (40%) of the title compound as a clear brown solid: mp (decomp) 221-223 ℃; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.75 - 7.86 (m, 3H), 7.63 - 7.73 (m, 4H), 7.50 - 7.63 (m, 4H), 7.45 (d, *J* = 1.5 Hz, 1H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.22 (td, *J* = 7.3, 1.0 Hz, 1H), 7.06 (t, *J* = 8.1 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 4.2 Hz, 1H), 5.57 (d, *J* = 7.6 Hz, 1H), 5.17 - 5.19 (m, 1H), 4.88 (d, *J* = 7.6 Hz, 1H), 2.88 (br. s, 1H); ^{13}C NMR (101 MHz, acetone-d_6) δ 149.5, 148.8, 148.1, 145.9, 144.9, 139.9, 136.5, 136.3, 133.2, 132.9, 130.6 (br.), 130.49 (q, $^3J_{C-F}$ = 10.8 Hz), 130.48, 130.3, 128.9, 128.3, 128.2, 128.1, 127.12, 127.09, 126.4-126.3 (m), 126.0, 124.2, 124.1, 123.0, 121.1, 121.0, 93.8, 91.2, 74.9, 74.0; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.48, -62.93; IR (KBr) ν_{max} 3336, 3067, 2920, 2851, 2220, 1927, 1616, 1571, 1518, 1476, 1458, 1407, 1326, 1174, 1129, 1105, 1069, 1033, 1027, 955, 845, 758, 740, 710, 603 cm^{-1}; HRMS (APCI) *m/z* for $C_{36}H_{21}O_2F_6$ $(M-H)^+$ calcd: 599.14403, found: 599.14372; R_f (5/2 hexanes/EtOAc) = 0.27.

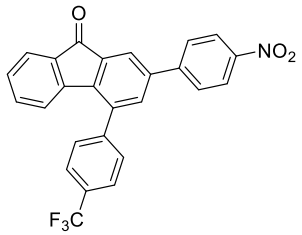


V Synthesis of 9,9'-spirobifluorenes 9

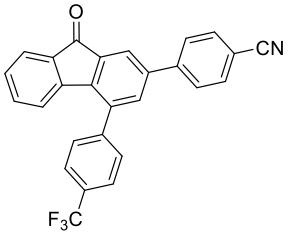
F_1: General procedure for oxidation reaction with PCC (preparation of 8). To a stirring solution of PCC (0.47 mmol, 102 mg, 1.5 eq.) and Celite® (100 mg) in anhydrous CH_2Cl_2 (0.021 M) the starting fluorenol **6** (0.31 mmol, 1.0 eq.) was added and the resulting reaction mixture was stirred for 3h at room temperature and under atmospheric conditions. The residue was filtered through a Celite®/silica gel plug and purified by column chromatography on silica gel to afford the corresponding fluorenone derivatives.

F_2: General procedure for oxidation reaction with MnO_2 (preparation of 8k) To a 0.02 M solution of the fluorenol **6k** in dry CH_2Cl_2 the commercially available active MnO_2 (10 eq.) was added. The suspension was vigorously shaken at room temperature for 20 h. The reaction mixture was filtered using a Celite® pad and purified by column chromatography on silica gel.

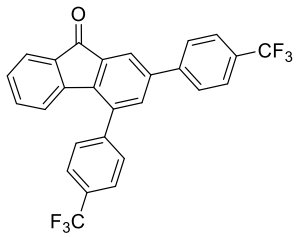
2-(4-Nitrophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8a). With **6a** (125 mg, 0.28 mmol) following the general procedure F_1. Column chromatography on silica gel (7/1 hexanes/EtOAc) gave 112 mg (90%) of the title compound as a bright orange solid: mp (decomp) 234-269 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 1.7 Hz, 1H), 7.77 - 7.87 (m, 4H), 7.70 - 7.75 (m, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 1.7 Hz, 1H), 7.23 - 7.33 (m, 2H), 6.73 - 6.81 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 147.6, 145.4, 143.4, 142.6, 141.2, 139.5, 137.2, 135.9, 135.0, 134.9, 134.6, 131.0 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.5, 129.3, 127.6, 126.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.7, 124.3, 124.0(q, $^1J_{C\text{-}F}$ = 271.1 Hz), 123.1, 122.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.50; IR (KBr) ν_{max} 3084, 3072, 1718, 1595, 1521, 1461, 1398, 1338, 1329, 1293, 1225, 1171, 1117, 1102, 1066, 1015, 958, 842, 812, 743, 689, 665 cm^{-1}; HRMS (APCI) *m/z* for $C_{26}H_{14}O_3NF_3$ $(M)^+$ calcd: 445.09203, found: 445.09165; R_f(7/1 hexanes/EtOAc) = 0.39.



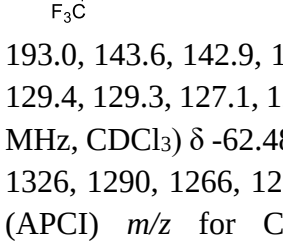
4-(9-Oxo-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-2-yl)benzonitrile (8b). With **6b** (30 mg, 0.07 mmol) following the general procedure F_1. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 22 mg (73%) of the title compound as a bright yellow solid: mp (decomp) 254-260 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.78-7.74 (m, 4H), 7.72-7.70 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.29-7.27 (m, 2H), 6.77-6.75 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 143.5, 143.4, 142.6, 141.0, 139.8, 137.1, 135.8, 134.9, 134.6, 132.8, 130.6 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.4, 129.3, 127.4, 125.9 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.7, 124.0 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 123.1, 122.6, 122.3, 118.6, 111.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.44; IR (KBr) ν_{max} 3058, 2956, 2923, 2854, 2232, 1715, 1601, 1577, 1467, 1404, 1323, 1296, 1213, 1171, 1129, 1108, 1078, 1063, 1021, 937, 854, 839, 818, 758, 701 cm^{-1}; HRMS (EI) *m/z* for $C_{27}H_{14}NOF_3$ $(M)^+$ calcd: 425.1027, found: 425.1025; R_f (3/1 hexanes/EtOAc) = 0.71.



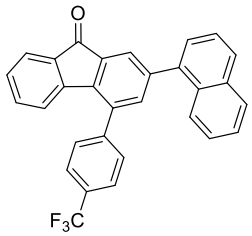
2,4-Bis(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8c). With **6c** (85 mg, 0.18 mmol) following the general procedure F_1. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 76 mg (90%) of the title compound as a bright yellow solid: mp (decomp) 179-182 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.96 Hz, 1H), 7.82 (d, *J* = 8.07 Hz, 2H), 7.70 - 7.78 (m, 5H), 7.67 (d, *J* = 8.07 Hz, 2H), 7.56 (d, *J* = 1.71 Hz, 1H), 7.23 - 7.31 (m, 2H), 6.72 - 6.79 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 143.6, 142.9, 142.6, 140.6, 140.5, 137.1, 135.8, 134.9, 134.8, 134.7, 130.9 - 130.1 (m), 129.4, 129.3, 127.1, 126.1 - 125.8 (m), 125.4 – 122.7 (m), 124.6, 123.0, 122.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.48, -62.53; IR (KBr) ν_{max} 3061, 2938, 1730, 1619, 1580, 1464, 1410, 1392, 1326, 1290, 1266, 1222, 1168, 1105, 1072, 1015, 958, 905, 839, 737, 707, 686 cm^{-1}; HRMS (APCI) *m/z* for $C_{27}H_{15}F_6O$ $(M+H)^+$ calcd: 469.10216, found: 469.10205; R_f (5/1 hexanes/EtOAc) = 0.67.



2-(4-Bromophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8d). With **6d** (83 mg, 0.17 mmol) following the general procedure F_1. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 68 mg (82%) of the title compound as a bright yellow solid: mp (decomp) 206-211 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 0.8 Hz, 1H), 7.81 (d, *J* = 5.2 Hz, 2H), 7.70-7.69 (m, 1H), 7.65 (d, *J* = 5.2 Hz, 2H), 7.58 (d, *J* = 6.0 Hz, 2H), 7.51-7.50 (m, 3H), 7.25-7,24 (m, 2H), 6.74-6.73 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 143.7, 142.9, 140.8, 140.0, 138.0, 137.0, 135.7, 134.6, 134.4, 132.1, 130.6 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.3, 129.1, 128.3, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.5, 124.01 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 122.9, 122.6, 122.5, 122.1; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.40; IR (KBr) ν_{max} 3073, 3058, 2962, 2923, 2851, 1978, 1942, 1909, 1715, 1607, 1577, 1497, 1461, 1404, 1329, 1296, 1231, 1165, 1120, 1102, 1075, 1012, 937, 854, 830, 806, 764, 737, 704 cm^{-1}; HRMS (EI) *m/z* for $C_{26}H_{14}OF_3Br$ $(M)^+$ calcd: 478.0180, found: 478.0181; R_f (10/1 hexanes/EtOAc) = 0.36 (silica gel plate).



2-(Naphth-1-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8e). With **6e** (66 mg, 0.14 mmol) following the general procedure F_1. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 53 mg (81%) of the title compound as a bright yellow solid: mp (decomp) 172-175 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98-7.87 (m, 4H), 7.80 (d, *J* = 8.00 Hz, 2H), 7.75-7.67 (m, 3H), 7.44-7.57 (m, 5H), 7.28-7.27 (m, 2H), 6.86-6.79 (m, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 143.9, 143.1, 141.9, 139.9, 138.2, 137.7, 136.5, 135.2, 134.7, 134.6, 133.9, 131.2, 130.5 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.4, 129.1, 128.5, 128.5, 126.9, 126.5, 126.1, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.5, 125.4, 125.3, 124.5, 124.1 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 122.9; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.46; IR (KBr) ν_{max} 3094, 3061, 3037, 2917, 2851, 2364, 2328, 1924, 1826, 1715, 1610, 1509, 1467, 1455, 1416, 1398, 1323, 1287, 1231, 1168, 1123, 1108,1066, 1024, 973, 949, 902, 851, 800, 782, 743, 686, 662 cm^{-1}; HRMS (APCI) *m/z* for $C_{30}H_{18}F_3O$ $(M+H)^+$ calcd: 451.13043, found: 451.13026; R_f (5/1 hexanes/EtOAc) = 0.62.



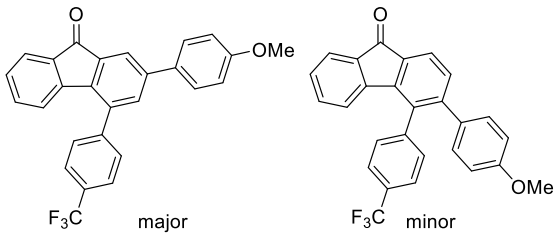
2-Phenyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8f). With **6f** (61 mg, 0.15 mmol) following the general procedure F_1. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 59 mg (98%) of the title compound as a bright yellow solid: mp (decomp) 174-178 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.0, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.71-7.69 (m, 1H), 7.68-7.64 (m, 4H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.25-7.23 (m, 2H), 6.76-6.73 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 143.9, 143.2, 142.1, 139.7, 139.1, 136.9, 135.7, 134.7, 134.6, 130.5 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 129.4, 129.02, 128.96, 128.2, 126.8, 125.8 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 124.7 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 124.5, 122.8, 122.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.45; IR (KBr) ν_{max} 3061, 2917, 2851, 1712, 1604, 1577, 1467, 1452, 1407, 1326, 1296, 1263, 1222, 1168, 1123, 1105, 1078, 1063, 1021, 955, 937, 893, 860, 842, 809, 755, 740, 698 cm^{-1}; HRMS (EI) *m/z* for $C_{26}H_{15}OF_3$ $(M)^+$ calcd: 400.1075, found: 400.1073; R_f (10/1 hexanes/EtOAc) = 0.62.

2-([1,1'-Biphenyl]-4-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8g). With **6g** (94 mg, 0.20 mmol) following the general procedure F_1. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 65 mg (70%) of the title compound as a bright yellow solid: mp (decomp) 132-138 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.75-7.63 (m, 9H), 7.60 (d, *J* = 1.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.26-7.24 (m, 2H), 6.76-6.74 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 143.9, 143.2, 141.6, 141.1, 140.3, 139.7, 137.9, 136.9, 135.7, 134.7, 134.7, 134.5, 134.5, 130.6 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 129.4, 129.0, 128.9, 127.7, 127.6, 127.1, 127.0, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.5, 124.1 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 122.8, 122.2; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.44; IR (KBr) ν_{max} 3061, 3031, 2926, 2854, 1718, 1604, 1574, 1488, 1464, 1443, 1404, 1326, 1293, 1231, 1162, 1132, 1108, 1066, 1024, 1006, 958, 934, 905, 857, 839, 812, 767, 734, 692 cm^{-1}; HRMS (EI) *m/z* for $C_{32}H_{19}OF_3$ $(M)^+$ calcd: 476.1388, found: 476.1374; R_f (10/1 hexanes/EtOAc) = 0.32 (silica gel plate).

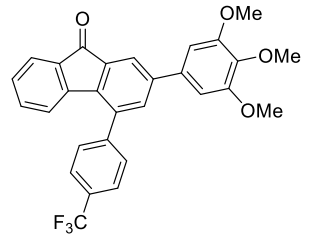
2-(*p*-Tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8h). With **6h** (215 mg, 0.52 mmol) following the general procedure F_1. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 180 mg (83%) of the two inseparable title regioisomer compounds in the ratio of 10:1 as a bright yellow solid. mp (decomp) 182-186 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.97 (d, *J* = 1.7 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.68 - 7.71 (m, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.55 (dt, *J* = 8.3, 2.0 Hz, 2H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.22 - 7.29 (m, 4H), 6.71 - 6.76 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 143.9, 143.3, 142.0, 139.4, 138.2, 136.8, 136.2, 135.7, 134.7, 134.6, 134.4, 130.5 (q, $^2J_{C\text{-}F}$ = 33.1 Hz), 129.7, 129.4, 128.9, 126.8 (q, $^1J_{C\text{-}F}$ = 270.1 Hz), 126.6, 125.8 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 124.4, 122.7, 122.2, 21.1; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.44; IR (KBr) ν_{max} 3058, 3031, 2917, 2863, 1963, 1906, 1712, 1607, 1577, 1518, 1461, 1410, 1395, 1329, 1293, 1225, 1159, 1123, 1102, 1066, 1021,

958, 902, 848, 821, 776, 746, 689, 656, 621, 600, 516, 474 cm^{-1}; HRMS (EI) *m/z* for $C_{27}H_{17}OF_3$ $(M)^+$ calcd: 414.1232, found: 414.1229; R_f (10/1 hexanes/EtOAc) = 0.46.

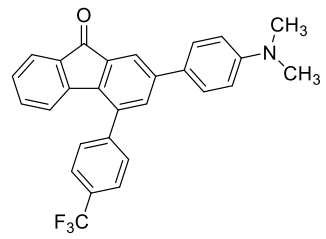
2-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8i). With **6i** (66 mg, 0.15 mmol) following the general procedure F_1. Column chromatography on silica gel (5/2 hexanes/EtOAc) gave 59 mg (89%) of the two inseparable title regioisomer compounds in the ratio of 10:1 of the title compound as a bright yellow solid: mp (decomp) 163-167 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.94 (d, *J* = 1.6, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.70-7.68 (m, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.24-7.22 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.72-6.71 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 159.9, 144.0, 141.7, 139.8, 139.0, 136.8, 135.7,134.7, 134.6, 134.1, 131.6, 130.6, 129.4, 128.8, 127.9, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.5, 122.7, 121.9, 114.4, 105.2, 55.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.44; IR (KBr) ν_{max} 3061, 3013, 2965, 2920, 2854, 1712, 1607, 1574, 1518, 1461, 1413, 1389, 1329, 1290, 1251, 1183, 1168, 1120, 1105, 1069, 1033, 1018, 955, 824, 737 cm^{-1}; HRMS (EI) *m/z* for $C_{27}H_{17}O_2F_3$ $(M)^+$ calcd: 430.1181, found: 430.1179; R_f (5/2 hexanes/EtOAc) = 0.52.



4-(4-(Trifluoromethyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-9*H*-fluoren-9-one(8j). With **6j** (172 mg, 0.35 mmol) following the general procedure F_1. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 130 mg (76%) of the title compound as a bright yellow solid: mp (decomp) 214-215 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.62 - 7.71 (m, 3H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.16 - 7.29 (m, 2H), 6.78 - 6.88 (m, 2H), 6.72 (m, *J* = 5.1 Hz, 1H), 3.93 (s, 6H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 153.6, 143.8, 143.1, 142.1, 139.6, 138.4, 136.8, 135.6, 134.9, 134.7, 134.6, 134.4, 130.6 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.3, 128.9, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.5, 124.0 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 122.8, 122.2, 104.0, 60.9, 56.3;^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.43; IR (KBr) ν_{max} 3004, 2938, 2836, 1718, 1607, 1589, 1518, 1464, 1434, 1410, 1359, 1326, 1234, 1165, 1126, 1072, 1009, 905, 851, 830, 743, 698, 665 cm^{-1}; HRMS (ESI) *m/z* for $C_{29}H_{22}O_4F_3$ $(M+H)^+$ calcd: 491.14647, found: 491.14628; R_f (3/1 hexanes/EtOAc) = 0.31.

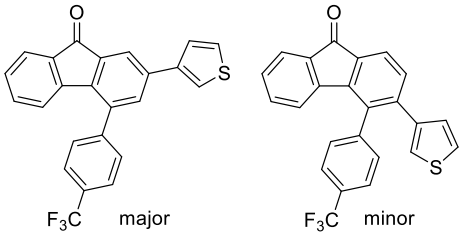


2-(4-(*N*,*N*-*D*imethylamino)phenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8k). With **6k** (92 mg, 0.21 mmol) following the general procedure F_2. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 77 mg (84%) of the title compound as a bright orange solid: mp (decomp) 186-190 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.7 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.62 - 7.69 (m, 3H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.19 - 7.22 (m, 2H), 6.82 (d, *J* = 6.1 Hz, 2H), 6.69 - 6.73 (m, 1H), 3.02 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 144.2, 143.6, 142.0, 138.2, 136.8, 135.7, 134.7, 134.5, 133.3, 130.7, 130.4 (q, $^2J_{C\text{-}F}$ = 32.2 Hz),

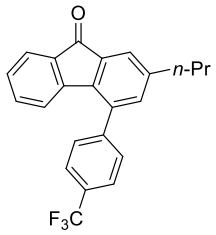


129.4, 128.9, 128.5, 127.4, 125.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.4, 124.1(q, $^{1}J_{C\text{-}F}$ = 270.4 Hz), 122.5, 121.4, 112.8, 43.6, 40.6; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.41; IR (KBr) ν_{max} 3052, 2965, 2920, 2890, 2854, 2800, 1954, 1924, 1718, 1601, 1533, 1461, 1413, 1368, 1326, 1287, 1234, 1195, 1168, 1120, 1108, 1066, 1021, 958, 884, 848, 815, 800, 740 cm^{-1}; HRMS (ESI) *m/z* for $C_{28}H_{21}ONF_3$ $(M+H)^+$ calcd: 444.15698, found: 444.15659; R_f (5/1 hexanes/EtOAc) = 0.26.

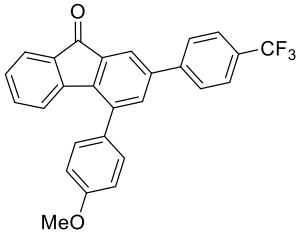
2-(Thien-3-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8l). With **6l** (65 mg, 0.16 mmol) following the general procedure F_1. Column chromatography on silica gel (5/2 hexanes/EtOAc) gave 58 mg (89%) of the two title regioisomer compounds in the ratio of 16:1 of the title compound as a bright yellow solid: mp (decomp) 163-171 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ = 7.91 (d, *J* = 1.6 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.67-7.62 (m, 3H), 7.54 (t, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 2H), 7.23-7.20 (m, 2H), 6.73-6.69 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 143.8, 143.06, 143.04, 140.2, 139.2, 136.8, 136.5, 135.5, 134.6, 134.5, 133.6, 130.4 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.3, 128.8, 126.8, 125.8 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.4, 124.0 (q, $^{1}J_{C\text{-}F}$ = 270.4 Hz), 122.6, 121.5, 121.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.34; IR (KBr) ν_{max} 3108, 3076 2932, 2851, 1930, 1712, 1604, 1574, 1533, 1464, 1413, 1326, 1165, 1111, 1078, 1063, 1018, 976, 934, 905, 848, 800, 782, 740, 710, 689, 668 cm^{-1}; HRMS (EI) *m/z* for $C_{24}H_{13}OSF_3$ $(M)^+$ calcd: 406.0639, found: 406.0642; R_f (5/2 hexanes/EtOAc) = 0.59.



2-Propyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8m). With **6m** (62 mg, 0.17 mmol) following the general procedure F_1. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 41 mg (70%) of the title compound as a bright yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.67 - 7.64 (m, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.17 - 7.23 (m, 2H), 7.11 (d, *J* = 1.6 Hz, 1H), 6.66 - 6.72 (m, 1H), 2.64 (t, *J* = 7.4 Hz, 2H), 1.69 (sxt, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 144.2, 144.2, 143.4, 138.6, 136.3, 135.1, 134.5, 134.5, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.3, 128.6, 128.2, 127.7, 125.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.3, 124.0, 122.5, 37.5, 24.2, 13.7; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.41; IR (KBr) ν_{max} 3315, 3070, 2965, 2932, 2875, 2854, 1718, 1607, 1467, 1329, 1287, 1242, 1189, 1174, 1111, 1069, 1015, 985, 923, 908, 857, 836, 743, 695, 659 cm^{-1}; HRMS (ESI) *m/z* for $C_{23}H_{17}F_3NaO$ $(M+Na)^+$ calcd: 389.112337, found: 389.112371; R_f (7/1 hexanes/EtOAc) = 0.64.

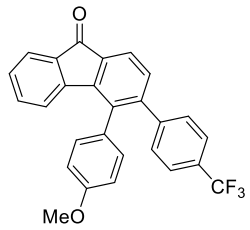


4-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8n). With **6n** (133 mg, 0.31 mmol) following the general procedure F_1. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 123 mg (92%) of the title compound as a bright yellow solid: mp (decomp) 165-166 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 1.6 Hz, 1H), 7.75 - 7.67 (m, 4H), 7.65 (m, *J* = 0.5 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.25 - 7.18 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.92 - 6.86 (m, 1H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 159.7, 144.2, 142.9,



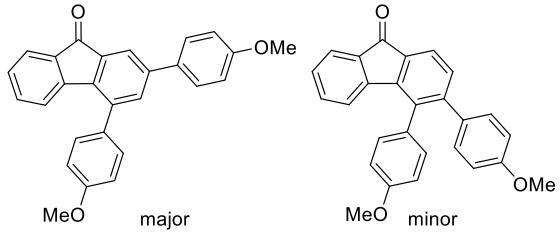
140.8, 140.0, 138.4, 135.6, 135.4, 134.6, 134.5, 131.2, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.9, 128.8, 127.0, 125.8 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.0 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 124.2, 123.2, 121.5, 114.2, 55.3; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.43; IR (KBr) ν_{max} 3393, 3073, 3058, 3034, 3007, 2965, 2941, 2911, 2839, 2543, 2528, 2098, 1909, 1870, 1832, 1709, 1604, 1577, 1521, 1464, 1416, 1404, 1323, 1290, 1251, 1204, 1168, 1123, 1114, 1084, 1069, 1036, 1015, 961, 937, 887, 860, 845, 812, 779, 758, 728, 704, 674, 626, 603 cm^{-1}; HRMS (APCI) *m/z* for $C_{27}H_{18}F_3O_2$ $(M+H)^+$ calcd: 431.12534, found: 431.12492; R_f (5/1 hexanes/EtOAc) = 0.40.

4-(4-Methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8n'). With **6n'**



(36.9 mg, 0.085 mmol) following the general procedure F_1. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 26.7 mg (73%) of the title compound as a bright yellow solid: mp (decomp) 209-211 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.3 Hz, 1H), 7.66 (dd, *J* = 7.1, 0.7 Hz, 1H), 7.45 (dd, *J* = 8.6, 0.7 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.18 - 7.24 (m, 3H), 7.15 (td, *J* = 7.6, 1.7 Hz, 1H), 7.07 (dt, *J* = 8.8, 2.7 Hz, 2H), 6.88 (dt, *J* = 8.8, 2.7 Hz, 2H), 6.35 (dt, *J* = 7.6, 0.9 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 159.2, 147.2, 144.5, 144.0 (q, $^{4}J_{C\text{-}F}$ = 1.5 Hz), 142.8, 136.3, 134.8, 134.5, 134.1, 131.0, 130.6, 129.8, 129.3, 129.1 (q, $^{2}J_{C\text{-}F}$ = 32.1 Hz), 128.7, 124.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.1, 124.1 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 123.4, 123.2, 114.1, 55.2; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.50; IR (KBr) ν_{max} 3392, 3092, 3051, 3012, 2968, 2917, 2841, 1708, 1603, 1575, 1515, 1464, 1404, 1321, 1283, 1245, 1166, 1109, 1062, 1033, 1014, 932, 834, 755, 694 cm^{-1}; HRMS (EI) *m/z* for $C_{27}H_{17}O_2F_3$ $(M)^+$ calcd: 430.1181, found: 430.1179; R_f (5/2 hexanes/EtOAc) = 0.46.

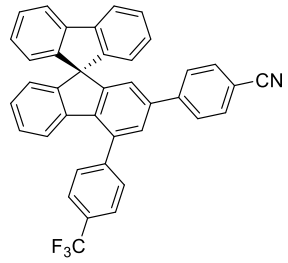
2,4-Bis(4-methoxyphenyl)-9*H*-fluoren-9-one (8o). With **6o** (106 mg, 0.27 mmol) following



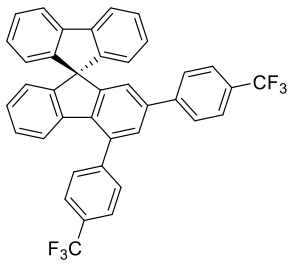
the general procedure F_1. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 97 mg (92%) of the two title regioisomer compounds in the ratio of 10:1 of the title compound as a bright yellow solid: mp (decomp) 86-90 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.67 - 7.63 (m, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.22 - 7.17 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.88 - 6.84 (m, 1H), 3.92 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 159.6, 159.5, 144.6, 141.3, 139.3, 138.2, 135.5, 134.70, 134.68, 134.4, 131.9, 131.8, 130.0, 128.3, 127.8, 124.1, 122.9, 121.1, 114.3, 114.1, 55.35, 55.33; ATR ν_{max} 3067, 3049, 3028, 3013, 2995, 2956, 2926, 2899, 2836, 1715, 1613, 1574, 1458, 1446, 1419, 1329, 1284, 1251, 1183, 1111, 1102, 1066, 1036, 955, 899, 839, 809, 773, 743, 689 cm^{-1}; HRMS (ESI) *m/z* for $C_{27}H_{20}O_3Na$ $(M+Na)^+$ calcd: 415.13047, found: 415.13081; R_f (5/1 hexanes/EtOAc) = 0.36.

G: General procedure for synthesis of 2,4-disubstituted-9,9'-spirobifluorene 9.[10] A dried Schlenk flask was filled up with 2-bromobiphenyl (0.55 mmol, 1.5 eq.) in anhydrous THF (0.05 M) and under argon atmosphere. The resulting solution was cooled down to -78 ℃ and *n*-BuLi (1.6 M in hexanes, 0.55 mmol, 1.5 eq.) was added dropwise. After stirring the solution for 30 min at -78 ℃, the fluorenone **8** (0.36 mmol, 1.0 eq.) in THF (0.03 M) was added dropwise and the reaction mixture was stirred for 15 min at -78 ℃. Then the reaction mixture was warmed up gradually to 25 ℃. After 4 hours, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with diethyl ether (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Silica gel column chromatography (10/1 hexanes/EtOAc) afforded the corresponding alcohol, which was subjected immediately to the next step. The alcohol was dissolved in acetic acid (0.02 M) and concentrated HCl (7 drops) was added. The resulting mixture was refluxed and after 3 hours was neutralized with saturated aqueous K_2CO_3 solution and extracted with diethyl ether (3 × 20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel provided the corresponding 9,9'-spirobifluorene compounds **9**.

4-(4-(4-(Trifluoromethyl)phenyl)-9,9'-spirobi[fluoren]-2-yl)benzonitrile (9b). With **8b** (77 mg, 0.18 mmol) following the general procedure G. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 50 mg (49%) of the title compound as a white solid: mp (decomp) 123-122 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, *J* = 8.1 Hz, 4H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.40 - 7.45 (m, 3H), 7.17 (td, *J* = 7.5, 1.0 Hz, 2H), 7.06 - 7.14 (m, 3H), 6.98 (d, *J* = 1.7 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.73 (dd, *J* = 6.4, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 149.6, 148.3, 144.6, 144.1, 141.8, 140.2, 139.1, 138.3, 136.7, 132.4, 130.3 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 129.7, 128.7, 128.3, 128.02, 128.00, 127.59, 127.55, 125.7 (q, ^3J = 3.8 Hz), 125.6, 124.2, 124.0, 122.8, 122.1, 120.2, 118.8, 110.9, 65.7; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.27; IR (KBr) ν_{max} 3061, 3040, 3019, 2929, 2229, 1604, 1512, 1446, 1410, 1389, 1329, 1261, 1251, 1222, 1171, 1132, 1108, 1066, 1018, 839, 752, 740, 677, 650 cm^{-1}; HRMS (APCI) *m/z* for $C_{39}H_{22}NF_3$ $(M)^+$ calcd: 561.16989, found: 561.16931; R_f(10/1 hexanes/EtOAc) = 0.40.



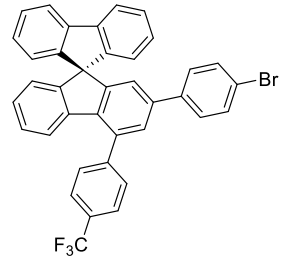
2,4-Bis(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9c). With **8c** (55 mg, 0.12 mmol) following the general procedure G. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 58 mg (81%) of the title compound as a white solid: mp (decomp) 184-187 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 - 7.91 (m, 4H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.50 - 7.58 (m, 4H), 7.38 - 7.44 (m, 3H), 7.16 (td, *J* = 7.5, 1.1 Hz, 2H), 7.06 - 7.13 (m, 2H), 7.03 (td, *J* = 7.6, 1.6 Hz, 1H), 6.97 (d, *J* = 1.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.73 (dd, *J* = 7.3, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 149.6, 148.5, 144.32, 144.30, 143.7, 141.8, 140.4, 139.0, 138.6, 136.6, 130.2 (q, $^2J_{C\text{-}F}$



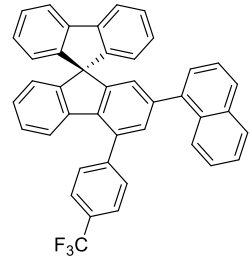
[10] Z. Jiang, H. Yao, Z. Zhang, C. Yang, Z. Liu, Y. Tao, J. Qin, D. Ma; *Org. Lett.* **2009**, *11*, 2607-2610.

= 32.2 Hz), 129.7, 129.4 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 128.8, 128.2, 128.0, 127.5, 127.3, 125.7 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 125.5 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 124.2, 124.1, 122.8, 122.3, 120.2, 65.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.30, -62.50; IR (KBr) ν_{max} 3064, 3043, 3013, 2929, 2851, 2361, 2325, 1954, 1921, 1616, 1571, 1479, 1449, 1410, 1392, 1326, 1278, 1245, 1171, 1123, 1066, 1018, 887, 842, 758, 743, 689, 653, 618 cm^{-1}; HRMS (APCI) *m/z* for $C_{39}H_{22}F_6$ $(M)^+$ calcd: 604.16202, found: 604.16138; R_f (10/1 hexanes/EtOAc) = 0.64.

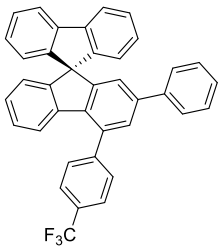
2-(4-Bromophenyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9d). With **8d** (68 mg, 0.14 mmol) following the general procedure G. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 33 mg (36%) of the title compound as a white solid: mp (decomp) 211-214 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 - 7.94 (m, 6H), 7.36 - 7.47 (m, 5H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.10 (td, *J* = 7.2, 1.2 Hz, 1H), 7.00 - 7.08 (m, 2H), 6.93 (d, *J* = 1.6 Hz, 1H), 6.85 (d, *J* = 7.2 Hz, 2H), 6.72 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 149.5, 148.6, 144.4, 141.8, 140.5, 139.2, 139.1, 138.1, 136.5, 131.7, 130.1 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.7, 128.6, 128.4, 128.01, 127.96, 127.9, 127.5, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.1, 122.9, 122.6, 121.9, 121.7, 120.1, 65.7; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.26; IR (KBr) ν_{max} 3067, 3040, 3016, 2923, 2851, 1619, 1598, 1583, 1494, 1479, 1449, 1404, 1383, 1326, 1278, 1248, 1165, 1123, 1105, 1069, 1021, 1009, 973, 961, 943, 926, 884, 851, 824, 782, 761, 743, 689, 656, 623 cm^{-1}; HRMS (APCI) *m/z* for $C_{38}H_{22}BrF_3$ $(M)^+$ calcd: 614.08515, found: 614.08531; R_f (10/1 hexanes/EtOAc) = 0.64.



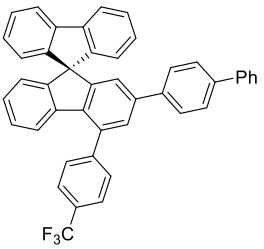
2-(Naphth-1-yl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9e). With **8e** (53 mg, 0.12 mmol) following the general procedure G. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 51 mg (74%) of the title compound as a white solid: mp (decomp) 142-144 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.80 (m, 7H), 7.77 (dd, *J* = 8.0, 5.3 Hz, 2H), 7.44-7.39 (m, 2H), 7.37 (dd, *J* = 7.6, 1.6 Hz, 3H), 7.34-7.28 (m, 2H), 7.18 (td, *J* = 7.5, 0.9 Hz, 2H), 7.15-7.05 (m, 3H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 1.6 Hz, 1H), 6.77 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 149.5, 148.6, 144.5, 141.8, 140.9, 139.9, 139.2, 137.5, 135.9, 133.7, 131.4, 131.3, 130.1, 129.8, 128.3, 127.88, 127.86, 127.83, 127.79, 127.4, 126.9, 126.0, 125.7, 125.6, 125.6 (q, $^{1}J_{C\text{-}F}$ = 3.8 Hz), 125.4, 125.2, 124.2, 124.0, 122.6, 120.1, 65.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.25; IR (KBr) ν_{max} 3058, 3040, 3019, 3010, 2950, 2923, 2851, 1619, 1509, 1476, 1449, 1392, 1326, 1281, 1242, 1168, 1129, 1108, 1084, 1066, 1021, 893, 845, 800, 779, 758, 740, 659 cm^{-1}; HRMS (APCI) *m/z* for $C_{42}H_{25}F_3$ $(M)^+$ calcd: 586.19029, found: 586.18954; R_f (10/1 hexanes/EtOAc) = 0.47.



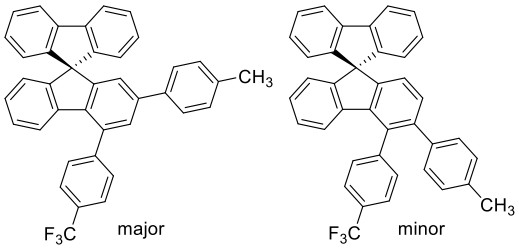
2-Phenyl-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9f). With **8f** (59 mg, 0.15 mmol) following the general procedure G. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 42 mg (53%) of the title compound as a white solid: mp (decomp) 147-150 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 - 7.90 (m, 6H), 7.37 - 7.45 (m, 5H), 7.31 (tt, *J* = 7.2, 1.6 Hz, 2H), 7.25 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.15 (td, *J* = 7.5, 1.1 Hz, 2H) 7.00 - 7.12 (m, 3H), 6.96 (d, *J* = 1.6 Hz, 1H), 6.86 (dt, *J* = 7.5, 0.9 Hz, 2H), 6.72 (d, *J* = 7.0 Hz, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 149.5, 148.7, 144.6, 141.8, 140.7, 140.5, 140.1, 137.6, 136.4, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.7, 128.6, 127.9, 127.8, 127.43, 127.39, 127.0, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.12, 124.09, 124.3 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 122.5, 122.2, 120.1, 65.7; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.18; IR (KBr) ν_{max} 3061, 1619, 1595, 1452, 1413, 1395, 1326, 1168, 1126, 1111, 1084, 1072, 1018, 887, 851, 755, 740, 695, 653, 626 cm^{-1}; HRMS (EI) *m/z* for $C_{38}H_{23}F_3$ $(M)^+$ calcd: 536.1752, found: 536.1749; R_f (10/1 hexanes/EtOAc) = 0.44.



2-([1,1'-Biphenyl]-4-yl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene]. (9g). With **8g** (65 mg, 0.14 mmol) following the general procedure G. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 32 mg (38%) of the title compound as a white solid: mp (decomp) 214-216 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 - 7.94 (m, 6H), 7.49 - 7.58 (m, 6H), 7.48 (d, *J* = 1.2 Hz, 1H), 7.37 - 7.45 (m, 4H), 7.33 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.16 (td, *J* = 7.6, 0.8 Hz, 2H), 7.11 (td, *J* = 7.6, 1.6 Hz, 1H), 7.02 - 7.08 (m, 2H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 149.5, 148.7, 144.6, 141.8, 140.6, 140.5, 140.3, 139.9, 139.0, 137.7, 136.4, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.7, 128.7, 128.5, 127.94, 127.86, 127.4, 127.3, 127.0, 126.9, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.13, 124.09, 124.3 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 122.6, 122.1, 120.1, 65.7; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.18; IR (KBr) ν_{max} 3058, 3028, 2926, 1613, 1598, 1488, 1473, 1446, 1413, 1392, 1309, 1284, 1168, 1120, 1111, 1066, 1021, 851, 836, 761, 743, 698, 674, 647, 623 cm^{-1}; HRMS (APCI) *m/z* for $C_{44}H_{27}F_3$ $(M)^+$ calcd: 612.20594, found: 612.20599; R_f (10/1 hexanes/EtOAc) = 0.42.

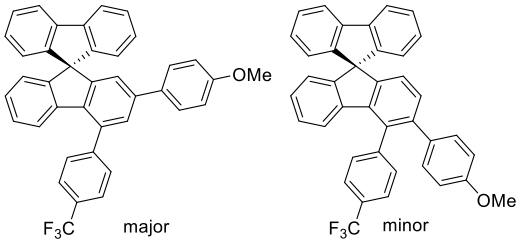


2-(p-Tolyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9h). With **8h** (151 mg, 0.36 mmol) following the general procedure G. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 98 mg (49%) of the two title regioisomer compounds in the ratio of 10:1 of the title compound as a white solid: mp (decomp) 132-138 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.84 - 7.94 (m, 5H), 7.39 - 7.46 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.26 (s, 1H), 7.09 - 7.20 (m, 5H), 7.06 (t, *J* = 6.4 Hz, 2H), 6.98 (d, *J* = 0.7 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 2H), 6.74 (d, *J* = 7.6 Hz, 1H), 2.33 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 149.5, 148.7, 144.7, 141.8, 140.7, 140.4, 137.35, 137.29, 137.2, 136.3, 131.0, 130.1, 129.7, 129.3, 128.4, 127.9, 127.8, 127.7, 127.4, 126.8, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.13, 124.06, 122.5, 122.0, 120.1, 65.7, 21.0; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.16; IR (KBr) ν_{max} 3047, 2923, 2870, 1913,1616, 1515, 1448, 1407,

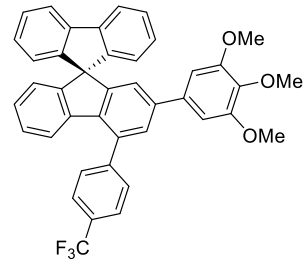


1321, 1280, 1252, 1163, 1125, 1103, 1065, 1017, 846, 812, 732 cm^{-1}; HRMS (EI) *m/z* for $C_{39}H_{25}F_3$ $(M)^+$ calcd: 550.1908, found: 550.1907; R_f(10/1 hexanes/EtOAc) = 0.41.

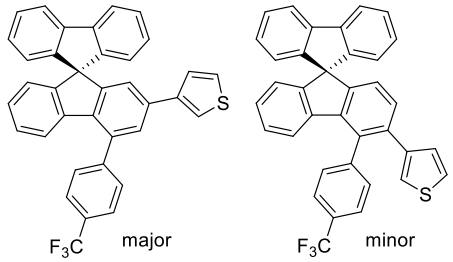
2-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9i). With **8i** (55 mg, 0.13 mmol) following the general procedure G. Column chromatography on silica gel (10/1 hexanes/ EtOAc) gave 65 mg (89%) of the two title regioisomer compounds in the ratio of 21:1 of the title compound as a white solid: mp (decomp) 131-134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.81 - 7.91 (m, 6H), 7.35 - 7.43 (m, 5H), 7.16 (td, *J* = 7.5, 1.1 Hz, 2H), 7.10 (td, *J* = 7.6, 1.2 Hz, 1H), 7.04 (td, *J* = 8.3, 1.6 Hz, 2H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.83 - 6.89 (m, 4H), 6.70 - 6.75 (m, 1H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 150.5, 149.4, 148.8, 144.7, 141.8, 140.8, 140.1, 137.0, 136.3, 132.6, 129.9 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.7, 128.1, 128.0, 127.9, 127.8, 127.7, 127.4, 125.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.1, 124.3 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 124.0, 122.4, 121.7, 120.1, 114.0, 65.7, 55.3; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.18; IR (KBr) ν_{max} 3050, 2961, 2936, 1606, 1578, 1515, 1445, 1318, 1287, 1245, 1166 1122, 1106, 1065, 1033, 1017, 881, 850, 831, 751, 736 cm^{-1}; HRMS (EI) *m/z* for $C_{39}H_{25}F_3O$ $(M)^+$ calcd: 566.1858, found: 566.1856; R_f(10/1 hexanes/EtOAc) = 0.32.



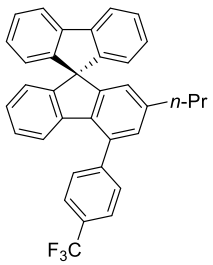
4-(4-(Trifluoromethyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-9,9'-spirobi[fluorene] (9j). With **8j** (130 mg, 0.27 mmol) following the general procedure G. Column chromatography on silica gel (3/1 hexanes/EtOAc) gave 136 mg (82%) of the title compound as a white solid: mp (decomp) 156-160 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 - 7.92 (m, 6H), 7.41 (td, *J* = 7.5, 1.1 Hz, 2H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.16 (td, *J* = 7.5, 1.1 Hz, 2H), 7.10 (td, *J* = 7.3, 1.5 Hz, 1H), 7.04 (td, *J* = 7.6, 1.5 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 1.7 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.70 (dd, *J* = 6.8, 1.0 Hz, 1H), 6.59 - 6.62 (m, 2H), 3.82 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 150.4, 149.6, 148.6, 144.58, 144.56, 141.8, 140.7, 140.5, 138.0, 137.8, 136.34, 136.32, 130.1 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 129.8, 128.6, 127.92, 127.85, 127.4, 125.6 (q, $^1J_{C\text{-}F}$ = 3.8 Hz),124.3 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 124.1, 124.0, 122.5, 122.2, 120.1, 104.7, 65.8, 60.9, 56.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.24; IR (KBr) ν_{max} 3073, 3040, 3013, 2962, 2941, 2842, 2827, 1616, 1583, 1509, 1443, 1404, 1362, 1329, 1275, 1242, 1165, 1132, 1117, 1105, 1063, 1006, 929, 908, 851, 836, 734, 668, 647, 615, 513, 489 cm^{-1}; HRMS (ESI) *m/z* for $C_{41}H_{29}O_3F_3Na$ $(M+Na)^+$ calcd: 649.19610, found: 649.19577; R_f(3/1 hexanes/EtOAc) = 0.34.



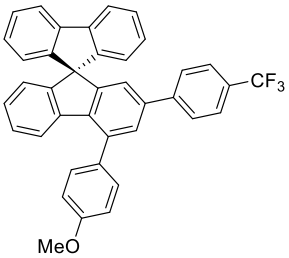
3-(4-(4-(Trifluoromethyl)phenyl)-9,9'-spirobi[fluoren]-2-yl)thiophene (9l). With **8l** (58 mg, 0.14 mmol) following the general procedure G. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 42 mg (53%) of the two title regioisomer compounds in the ratio of 17:1 of the title compound as a white solid: mp (decomp) 140-142 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.78 - 7.91 (m, 6H), 7.36 - 7.45 (m, 3H), 7.30 (dd, *J* = 3.2, 1.5 Hz, 1H), 7.25 - 7.28 (m, 1H), 7.22 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.15 (td, *J* = 7.2, 0.8 Hz, 2H), 7.09 (td, *J* = 7.6, 1.5 Hz, 1H), 6.98 - 7.06 (m, 2H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.85 (dt, *J* = 7.6, 0.9 Hz, 2H), 6.69 - 6.72 (m, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 149.5, 148.7, 144.6, 141.8, 141.4, 140.7, 137.5, 136.4, 135.1, 130.7, 130.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 129.7, 127.94, 127.90, 127.86, 127.8, 127.4, 126.21, 126.18, 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.12, 124.05, 122.5, 121.5, 120.7, 120.1, 65.7; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.24; IR (KBr) ν_{max} 3100, 3067, 3046, 3016, 2926, 2857, 1622, 1601, 1583, 1446, 1404, 1326, 1281, 1248, 1171, 1120, 1108, 1084, 1066, 1018, 982, 934, 908, 884, 866, 851, 782, 755, 740, 647 cm^{-1}; HRMS (APCI) *m/z* for $C_{36}H_{21}F_3S$ $(M)^+$ calcd: 542.13106, found: 542.13073; R_f (10/1 hexanes/EtOAc) = 0.63.



2-Propyl-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9m). With **8m** (27 mg, 0.07 mmol) following the general procedure G. Column chromatography on silica gel (10/1 hexanes/EtOAc) gave 18 mg (50%) of the title compound as a white solid: mp (decomp) 81-83 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.39 (td, *J* = 7.6, 1.0 Hz, 2H), 7.15 (td, *J* = 7.5, 1.1 Hz, 2H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 6.96 - 7.02 (m, 3H), 6.81 (d, *J* = 7.6 Hz, 2H), 6.65 - 6.70 (m, 1H), 6.56 (d, *J* = 1.5 Hz, 1H), 2.45 (t, *J* = 8.1 Hz, 2H), 1.50 (sxt, *J* = 8.0 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.2, 149.1, 144.9, 142.5, 141.8, 141.1, 136.1, 135.8, 129.9, 129.8, 129.7, 127.8, 127.7, 127.3, 127.2, 125.4 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.1, 124.4 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 124.0, 123.7, 122.2, 120.0, 65.6, 37.8, 24.4, 13.8; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.24; IR (KBr) ν_{max} 3060, 2958, 2923, 2866, 1948, 1923, 1616, 1587, 1515, 1448, 1416, 1397, 1318, 1277, 1245, 1163, 1119, 1106, 1065, 1017, 935, 894, 846, 799, 761, 739, 682 cm^{-1}; HRMS (CI) *m/z* for $C_{35}H_{26}F_3$ $(M+H)^+$ calcd: 503.1987, found: 503.1985; R_f (10/1 hexanes/EtOAc) = 0.70.

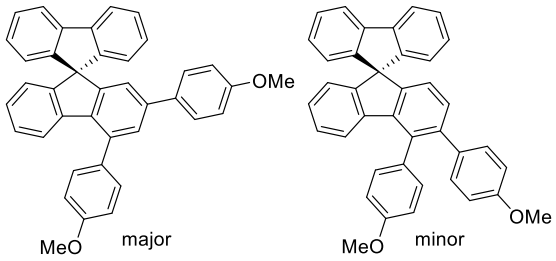


4-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9n). With **8n** (123 mg, 0.28 mmol) following the general procedure G. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 144 mg (89%) of the title compound as a white solid: mp (decomp) 133-135 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.53 (s, 4H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.40 (td, *J* = 7.5, 0.8 Hz, 2H), 7.07 - 7.18 (m, 6H), 7.04 (td, *J* = 7.2, 1.2 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 7.2 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 150.5, 149.5, 148.8, 144.1, 141.8, 141.0, 139.0, 138.7, 138.0, 132.9, 130.3, 129.1, 129.0, 127.9, 127.84, 127.77, 127.34, 127.30, 125.5,



125.5 (q, J = 3.8 Hz), 124.1, 123.9, 123.1, 121.4, 120.1, 114.1, 65.8, 55.4; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -62.45; IR (KBr) ν_{max} 3058, 3037, 3013, 2956, 2932, 2905, 2836, 1613, 1574, 1515, 1446, 1395, 1329, 1293, 1245, 1165, 1129, 1075, 1060, 1033, 1015, 1003, 964, 952, 923, 887, 839, 758, 740, 674, 659, 621, 579 cm^{-1}; HRMS (APCI) *m/z* for $C_{39}H_{25}OF_3$ $(M)^+$ calcd: 566.18520, found: 566.18524; R_f (10/1 hexanes/EtOAc) = 0.22.

2,4-Bis(4-methoxyphenyl)-9,9'-spirobi[fluorene] (9o). With **8o** (92 mg, 0.24 mmol) following the general procedure G. Column chromatography on silica gel (5/1 hexanes/EtOAc) gave 83 mg (67%) of the two title regioisomer compounds in the ratio of 9:1 of the title compound as a white solid: mp (decomp) 141-142 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) (major) δ 7.87 (dt, J = 7.6, 0.9 Hz, 2H), 7.60 (dt, J = 8.6, 2.0 Hz, 2H), 7.35 - 7.41 (m, 5H), 7.10 - 7.19 (m, 5H), 7.07 (td, J = 7.5, 1.3 Hz, 1H), 7.01 (td, J = 7.3, 1.2 Hz, 1H), 6.81 - 6.88 (m, 5H), 6.69 (d, J = 7.2 Hz, 1H), 3.96 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 159.1, 150.1, 149.3, 149.1, 141.8, 141.4, 139.8, 137.7, 137.5, 133.4, 133.1, 131.5, 131.0, 130.4, 128.5, 128.0, 127.9, 127.7, 127.3, 127.2, 124.2, 123.8, 122.7, 120.8, 120.0, 114.0, 113.9, 65.8, 55.4, 55.3; IR (KBr) ν_{max} 3064, 3040, 3013, 2947, 2932, 2905, 2839, 1607, 1577, 1515, 1449, 1437, 1392, 1287, 1245, 1180, 1156, 1108, 1066, 1030, 1003, 970, 949, 926, 884, 839, 806, 779, 758, 740, 689, 671, 653, 623, 576 cm^{-1}; HRMS (APCI) *m/z* for $C_{39}H_{29}O_2$ $(M+H)^+$ calcd: 529.21621, found: 529.21654; R_f (5/1 hexanes/EtOAc) = 0.47.



VI X-ray analysis

Whole sets of diffraction data for all crystals were collected on diffractometer Bruker D8 VENTURE Kappa Duo PHOTON100 by IμS micro-focus sealed tube either MoKα (λ= 0.71073) or CuKα (λ = 1.54178 Å) at low temperature. The structures were solved by direct methods (XT)[11] and refined by full matrix least squares based on F^2 (SHELXL2018)[12]. The hydrogen atoms on carbon were calculated into idealized positions and fixed during refinement (riding model with assigned temperature factors either $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or $H_{iso}(H) = 1.5\ U_{eq}$ (pivot atom) for methyl moiety. Several crystals require special approaches during structure determination:

SI-Table 1. X-ray data for **4d'**, **9c**, **9g**, **9h'**, **9h**, **9i** and **9n.**

Compound	**4d' (FS_31)**	**9c (IC55)**	**9g (IC33)**
CCDC no.	1956788	1956789	1956790
Formula	$C_{33}H_{24}O$	$C_{39}H_{22}F_6$	$C_{44}H_{27}F_3$
M.w.	436.52	604.56	612.65
Temperature [K]	150	120	120
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group [No.]	*P*-1(No 2)	$P2_1/c$ (No 14)	$Pna2_1$ (No 33)
a [Å]	10.4570 (7)	16.8872 (9)	14.2751 (4)
b [Å]	10.5521 (8)	21.0058 (11)	15.2598 (5)
c [Å]	11.5509 (9)	8.4685 (4)	28.0331 (8)
α [°]	98.573 (3)		
β [°]	109.660 (2)	91.780 (2)	
γ [°]	100.443 (2)		
Z	2	4	8
V *[Å³]*	1149.62 (15)	3002.6 (3)	6106.6 (3)
D_x [g cm^{-3}]	1.261	1.337	1.333
Crystal size [mm]	0.36 ×0.21 ×0.08	0.30 ×0.08 ×0.05	0.27 ×0.17 ×0.11
Crystal shape, colour	Prism,yellow	Bar, colourless	Prism, colourless
μ [mm^{-1}]	0.07	0.87	0.72
θ_{max} [°]	27.5	70.2	72.2
Range of *h*;*k*;*l*	-13,12; -13,13; -14,14	-20,20; -25,25; -10,10	-17,17; -18,18; -34,33
Measured reflections	45217	35222	79931
Independent diffractions (R_{int} [a])	5273 (0.031)	5726 (0.039)	11866 (0.035)
Observed diffract. [$I>2\sigma(I)$]	4641	4913	11378
T_{min}, T_{max}	0.97, 0.99	0.81, 0.96	0.85, 0.93
No. of parameters	309	434	866
w_1, w_2 [b]	0.0547, 0.547	0.0499, 2.0128	0.0447, 1.2767
Absolut. structure param. (Flack)			-0.05 (4)
R[c] [$F^2 > 2\sigma(F^2)$]	0.042	0.045	0.032
w$R(F^2)$ for all data	0.113	0.114	0.081
GOF [d]	1.05	1.06	1.06
Residual electron density [e/Å^3]	0.30, -0.23	0.48, -0.44	0.25, -0.26

[11] SHELXT: Sheldrick, G.M. (2015). *Acta Cryst*. **A71**, 3-8.
[12] SHELXL: Sheldrick, G.M. (2015). *Acta Cryst.* **C71**, 3-8.

9h' (IC27b)	**9h (IC27)**	**9i (IC29)**	**9n (IC75)**
1956791	1956792	1956793	1956794
$C_{39}H_{25}F_3$	$C_{39}H_{25}F_3$	$C_{39}H_{25}F_3O$	$C_{39}H_{25}F_3O$
550.59	550.59	566.59	566.59
120	120	120	120
Monoclinic	Triclinic	Monoclinic	Triclinic
$P2_1/n$ (No 14)	P-1 (No 2)	$P2_1/n$ (No 14)	P -1 (No 2)
18.922 (2)	9.5837 (6)	13.7277 (8)	20.4066 (10)
13.2624 (16)	15.8755 (10)	23.9445 (12)	21.8326 (10)
23.781 (3)	19.7226 (12)	18.2192 (10)	23.9536 (10)
	88.769 (2)		113.321 (2)
110.347 (4)	79.277 (2)	108.198 (2)	99.652 (2)
	74.289 (2)		110.445 (2)
8	4	8	12
5595.7 (12)	2836.8 (3)	5689.2 (5)	8582.7 (7)
1.307	1.289	1.323	1.315
0.39 ×0.30 ×0.26	0.68 ×0.25 ×0.08	0.22 ×0.21 ×0.10	0.61 ×0.47 ×0.19
Prism,colourless	Prism,colourless	Prism, colourless	Plate, colourless
0.09	0.09	0.09	0.09
27.5	26.1	26.1	27.6
-24,24; -17,16;	-11,9; -19,19;	-16,16;-29,25;	-26,26;-28,28;
-30, 30	-24,24	-22, 22	-31, 31
85666	65498	78453	203837
12854 (0.034)	11180 (0.037)	11192 (0.083)	39562 (0.039)
10579	9088	7319	29480
0.95, 0.98	0.94,0.99	0.92, 0.99	0.92, 0.98
873	794	777	2362
0.0556, 2.794	0.048, 1.7109	0.0482, 2.4483	0.0725, 8.9884
0.046	0.046	0.050	0.063
0.120	0.117	0.118	0.169
1.04	1.05	1.03	1.01
0.30, -0.29	0.31, -0.36	0.37, -0.35	1.14, -1.08

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$, [b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = \_[\max(F_o^2,0) + 2F_c^2]/3$. [c] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$. [d] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$.

Further comments of crystal structures.

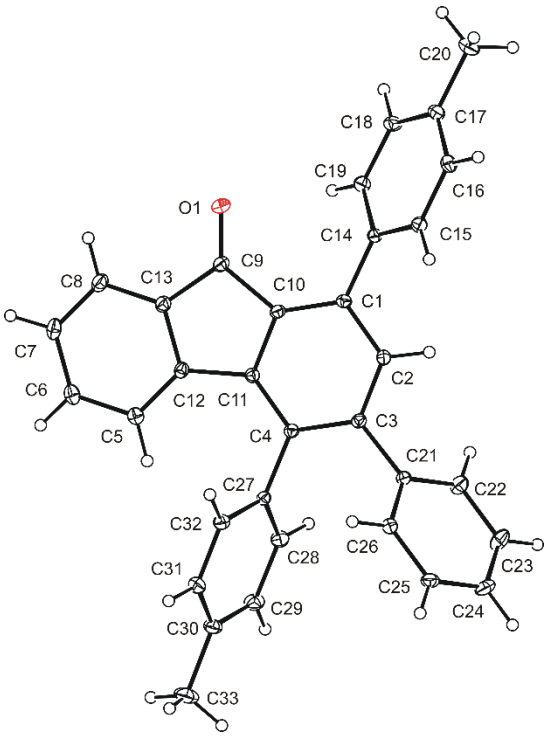
9c (IC55) The structure determination is complicated by disorder of one $–CF_3$ described by two position of each fluorine atoms with ration of occupancy factors 0.617:383. During refinement several parameters of disordered atoms needs to restricted. The contribution of disordered solvent was removed from diffraction data via PLATON /SQUEEZE procedure to enhance ability to resolve disorder of main molecule.

9g (IC33) The unit cell of IC_33 contains two symmetrically independent molecules from which one exhibits disorder of $–CF_3$ moiety, hampering overall precision of results.

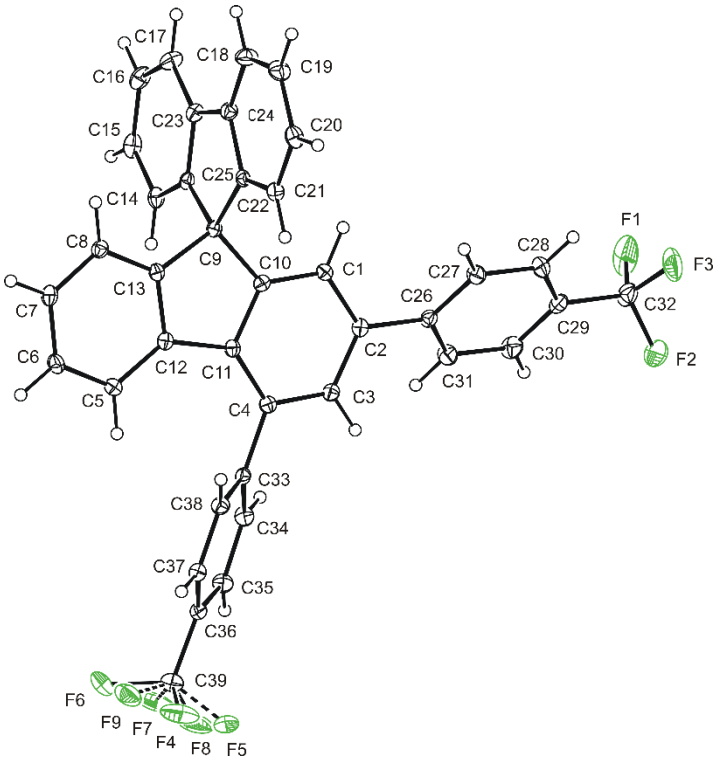
9h' (IC27b) Two symmetrically independent molecules in unit cell with disordered $–CF_3$ moieties, has to be refined with restriction of occupancy and displacement factors of fluorine atoms.

9h (IC27) In this case, the $–CF_3$ moieties are ordered, however the position of one of symmetrically molecules appears to be occupied by two isomers with ration 0.646 :0.354.

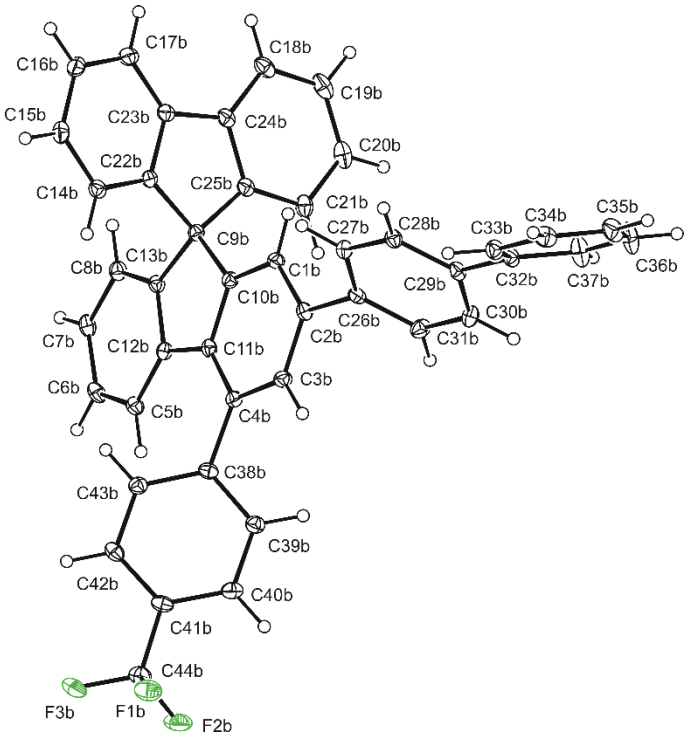
9n (IC75) The most difficult structure from whole series. Six symmetrically independent molecules in the unit cell one more disordered than others with overall large displacement parameters of most of the atoms decrease ability of the crystal to diffract. The poor quality of the crystal triggered on several alerts during validation. However we decided to include this structure in the paper to complete the series of synthesized compound.



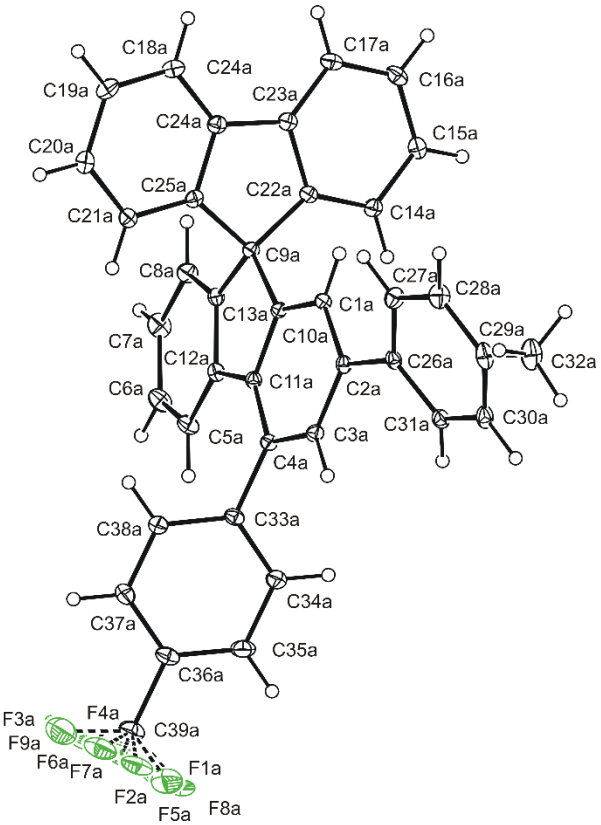
SI-Figure 1. ORTEP drawing of **4d'** with 30% probability.



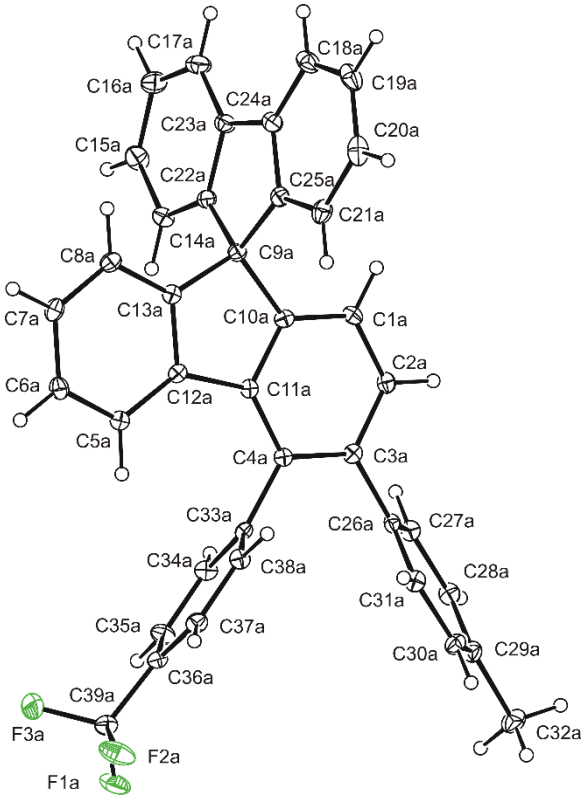
SI-Figure 2. ORTEP drawing of **9c** with 30% probability.



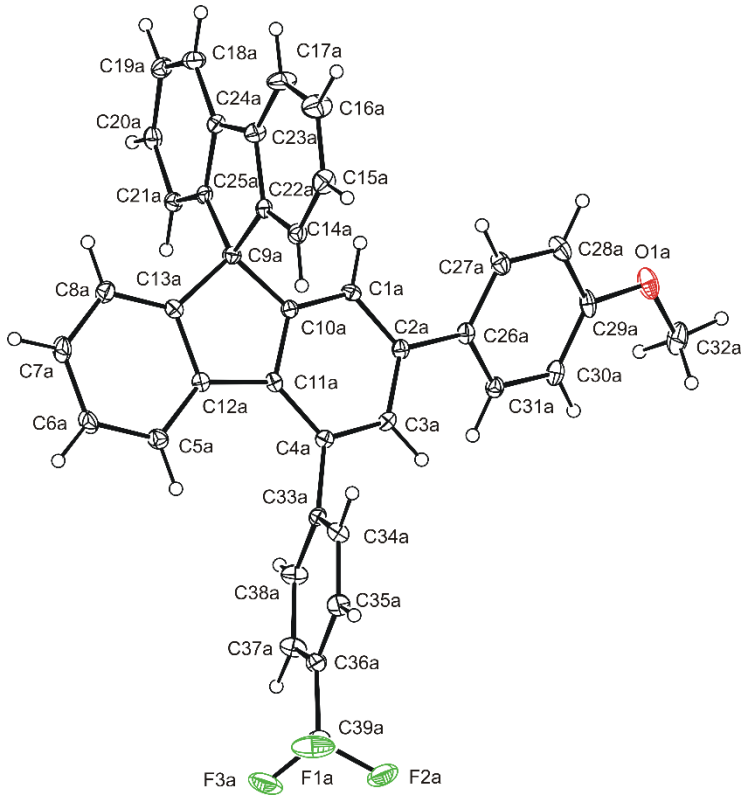
SI-Figure 3. ORTEP drawing of **9g** with 30% probability.



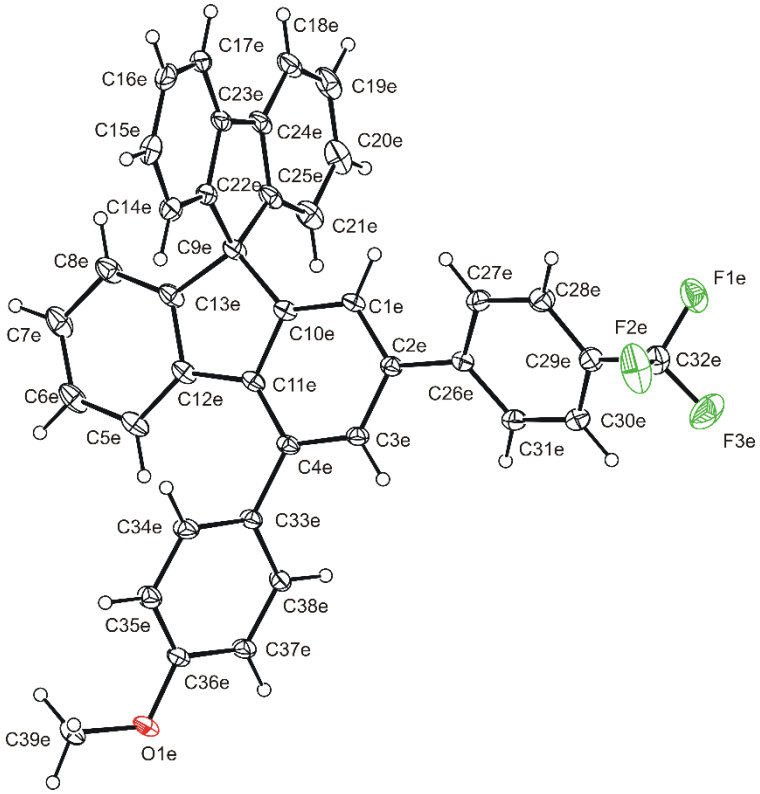
SI-Figure 4. ORTEP drawing of **9h'** with 30% probability.



SI-Figure 5. ORTEP drawing of **9h** with 30% probability.



SI-Figure 6. ORTEP drawing of **9i** with 30% probability.



SI-Figure 7. ORTEP drawing of **9n** with 30% probability.

VII Photophysical properties

UV/Vis absorption and emission spectroscopy.

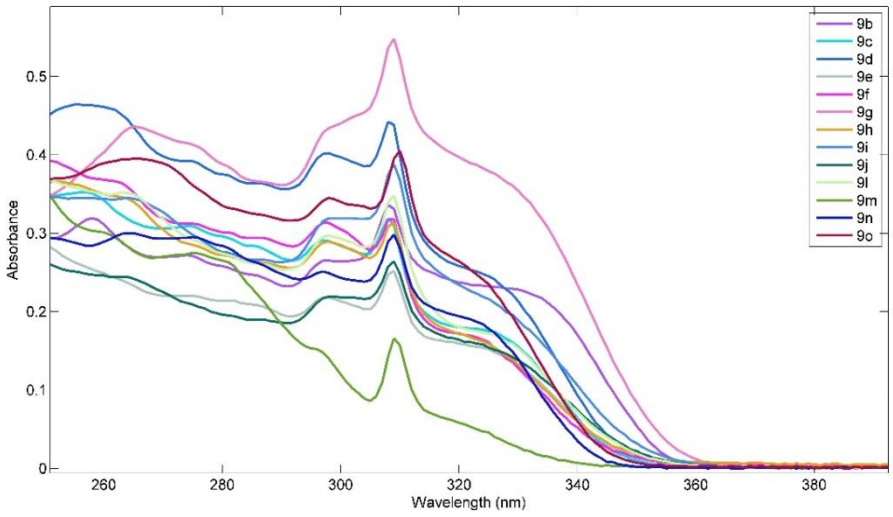
The UV/Vis absorption spectra were recorded using Unicam 340 spectrometer. Corrected steady-state emission spectra were recorded on an Aminco Bowman (AB2) spectrometer. Absolute quantum yields of fluorescence were recorded on Quantaurus-QY Plus UV-NIR absolute PL quantum yield spectrometer (Hamamatsu), using λ = 280 nm as excitation wavelength.

Micromolar solutions of the samples were prepared in cyclohexane.

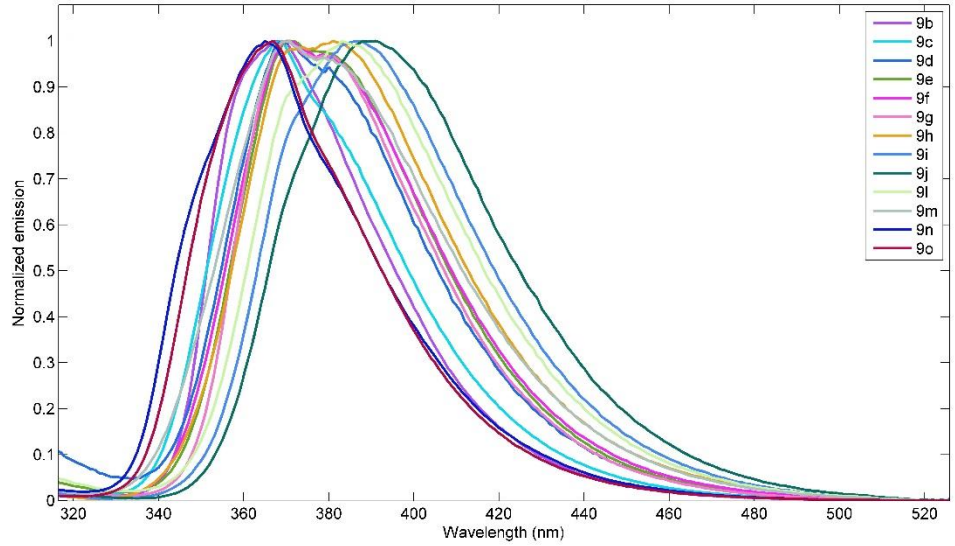
SI-Table 2. Photophysical properties of **9** derivatives in cyclohexane.

9	λ_{abs}/nm ($\varepsilon/10^4$ $mol^{-1}\cdot dm^3\cdot cm^{-1}$)	λ_{em}/nm	Φ_s[a]
9b	258 (3.1), 274 (sh), 297 (2.6), 308 (3.3), 331 (sh)	367	0.92
9c	256 (3.5), 274 (sh), 297 (2.9), 308 (3.2), 326 (sh)	368, 378	0.88
9d	258 (4.6), 275 (sh), 298 (4.0), 308 (4.4), 326 (sh)	369, 380	0.14
9e	255 (sh), 275 (sh), 297 (2.1), 309 (2.4), 323 (sh)	371, 379	0.77
9f	250 (sh), 262 (sh), 297 (3.1), 309 (3.1), 323 (sh)	370. 379	0.86
9g	265(4.4), 275 (sh), 298 (sh), 309 (5.5), 326 (sh)	370, 380	1.00
9h	252 (sh), 263 (sh), 298 (2.9), 309 (3.1), 325 (sh)	373, 380	0.69
9i	264 (sh), 299 (3.2), 309 (3.9), 323 (sh)	386	0.78
9j	264 (sh), 298 (2.2), 309 (2.7), 324 (sh)	391	0.37
9l	264 (3.5), 298 (3.0), 309 (3.5), 326 (sh)	372, 385	0.44
9m	260 (sh), 278 (2.5), 297 (sh), 309 (1.6)	370, 380	0.64
9n	264 (3.0), 275 (sh), 297 (2.5), 309 (3.0), 323 (sh)	365	0.86
9o	265 (3.9), 298 (3.4), 310 (4.0), 323 (sh)	367	0.91

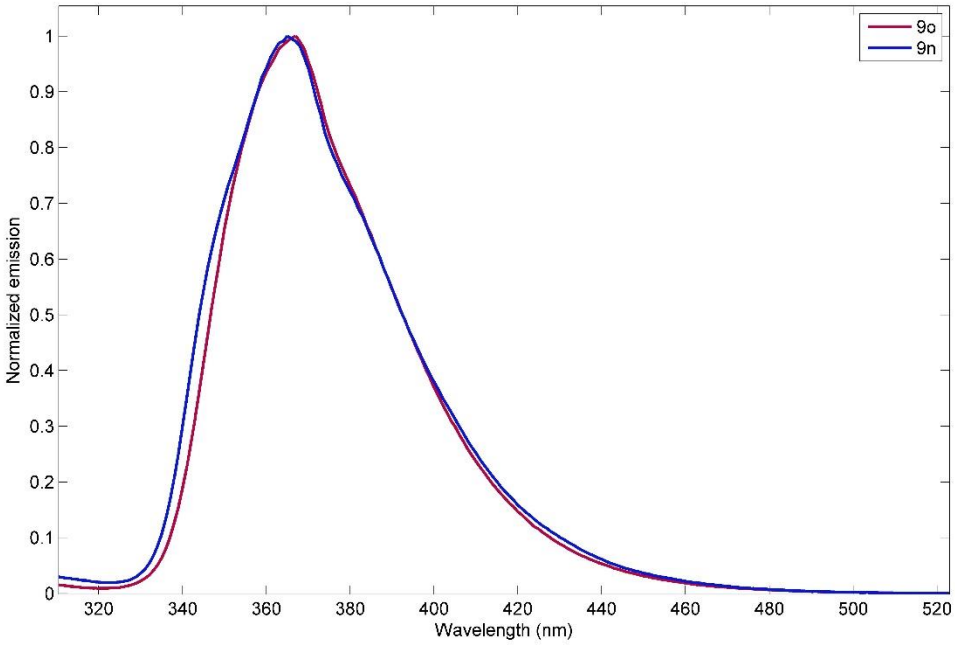
[a] Absolute quantum yield, λ_{exc}= 280 nm.



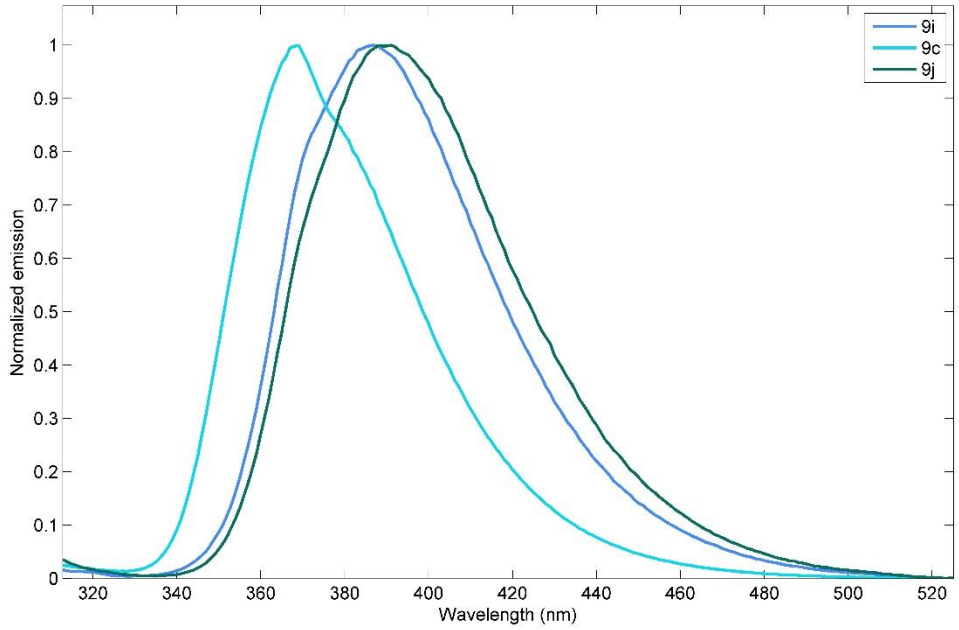
SI-Figure 8. Absorption spectra of **9** (10^{-5}M) in cyclohexane.



SI-Figure 9. Normalized emission spectra of **9** (10^{-6}M) in cyclohexane.



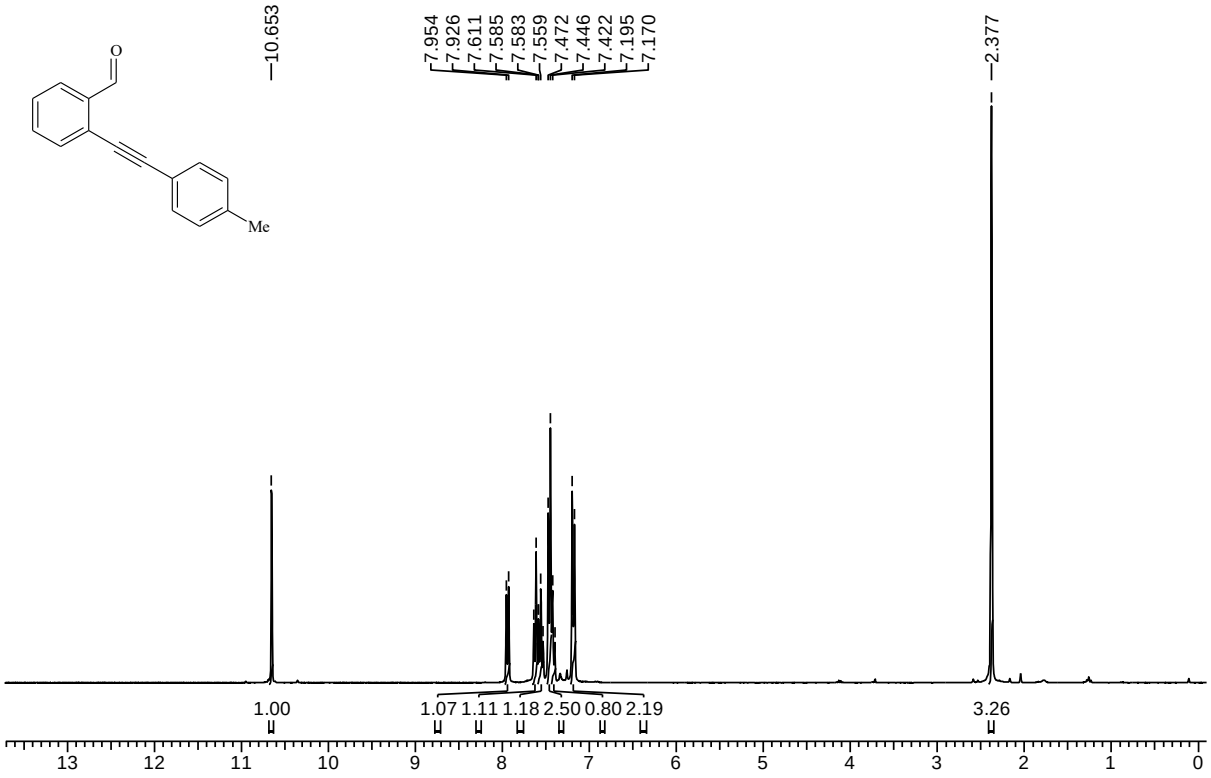
SI-Figure 10. Normalized emission spectra of **9n** *vs* **9o** (10^{-6}M) in cyclohexane.

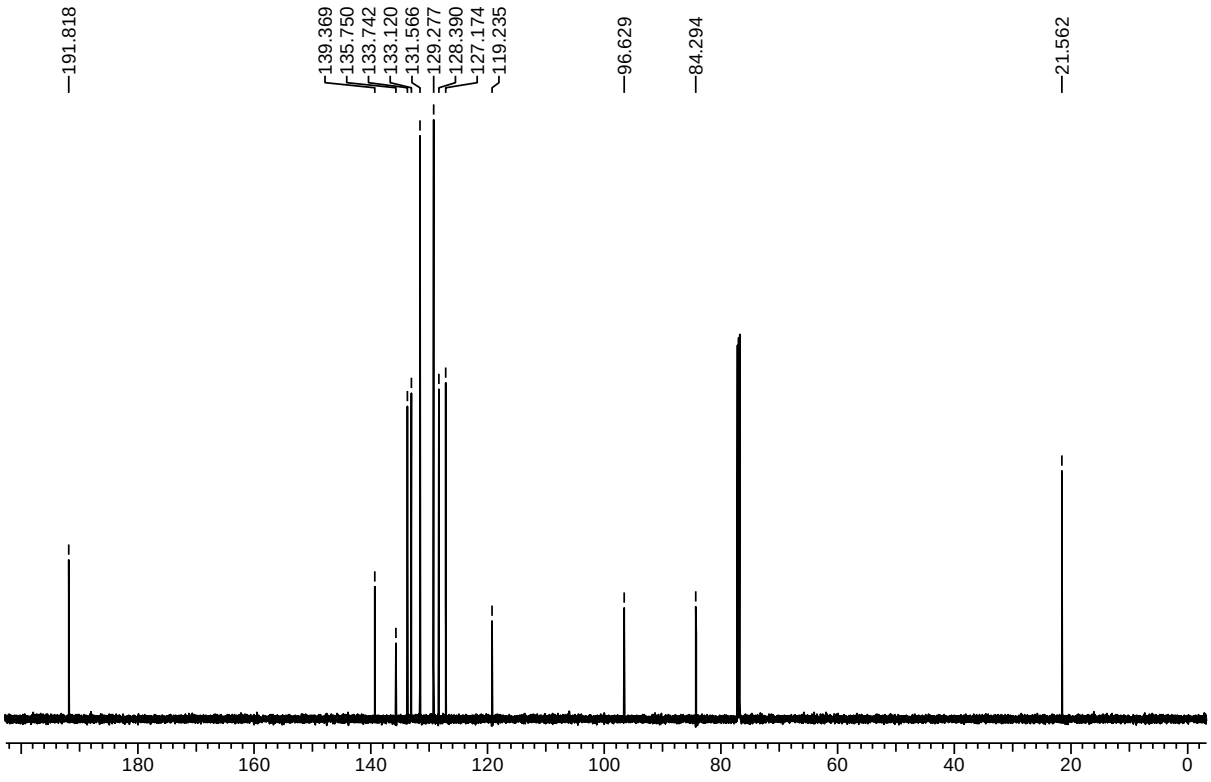


SI-Figure 11. Normalized emission spectra of **9c** *vs* **9i** *vs* **9j** (10^{-6}M) in cyclohexane.

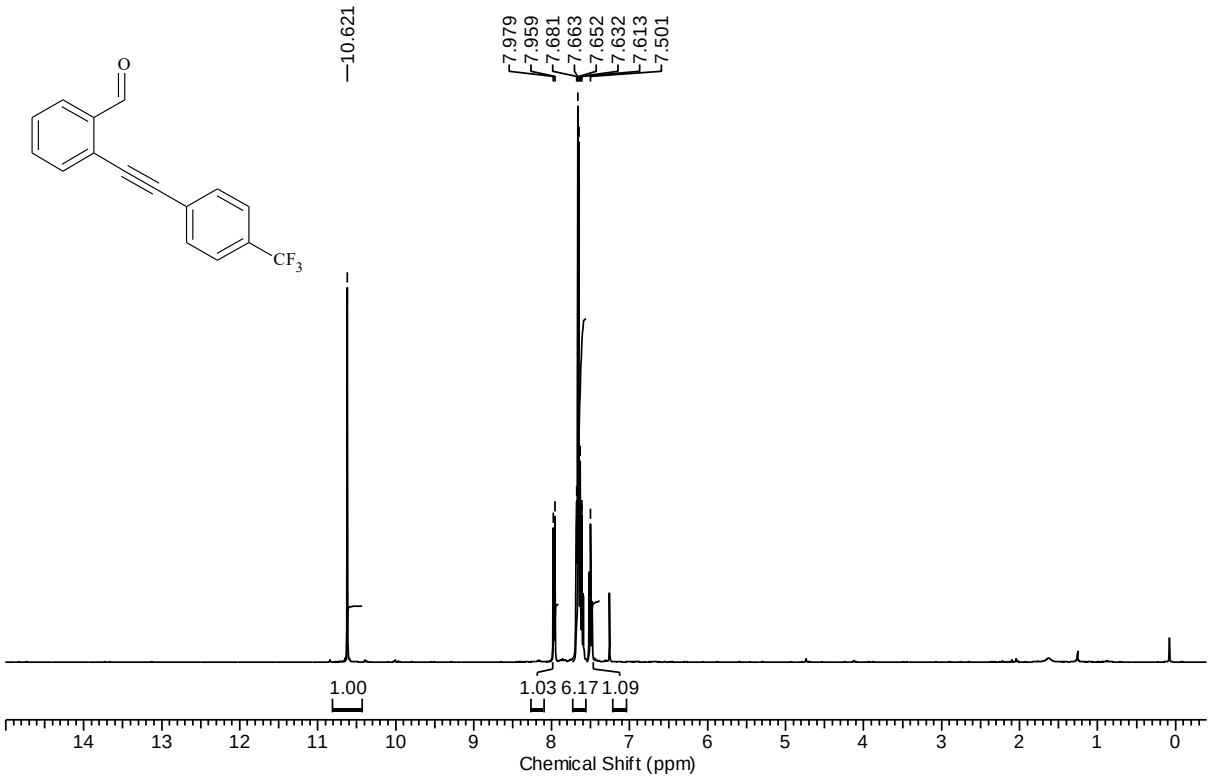
VIII Copies of ^{1}H and ^{13}C NMR spectra

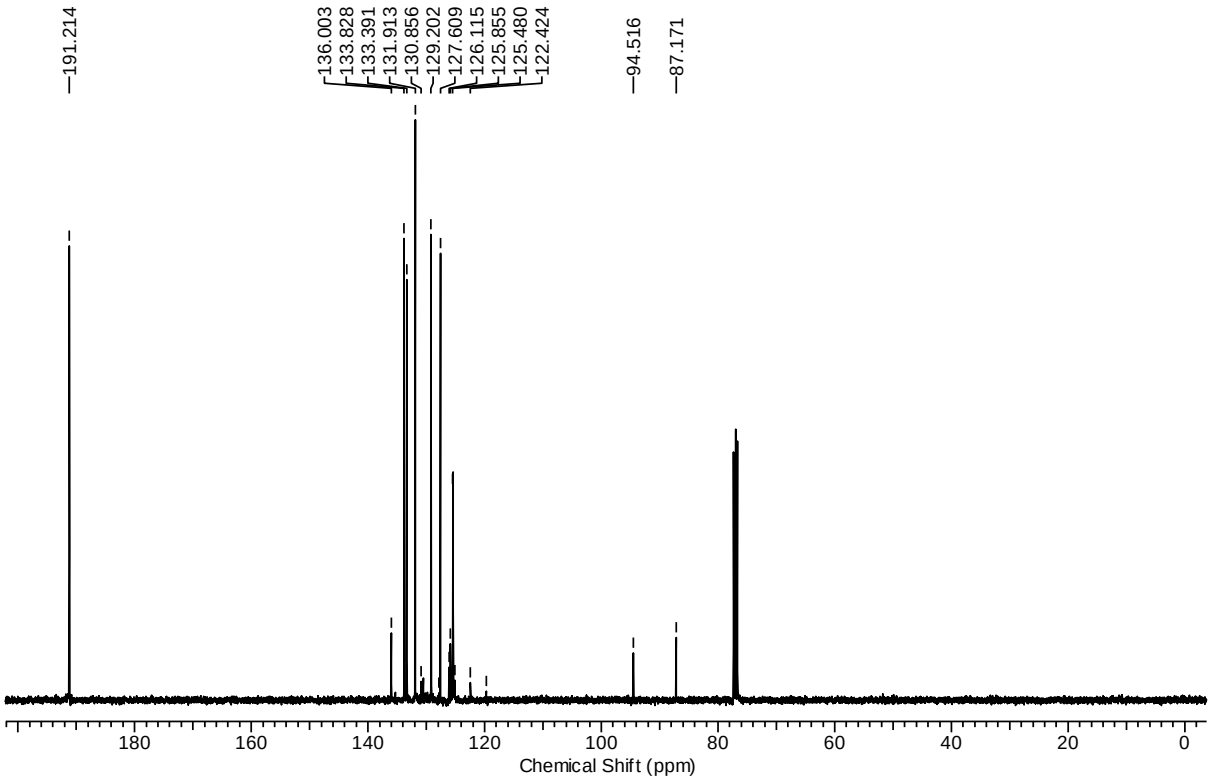
2-(*p*-Tolylethynyl)benzaldehyde (S-1a)



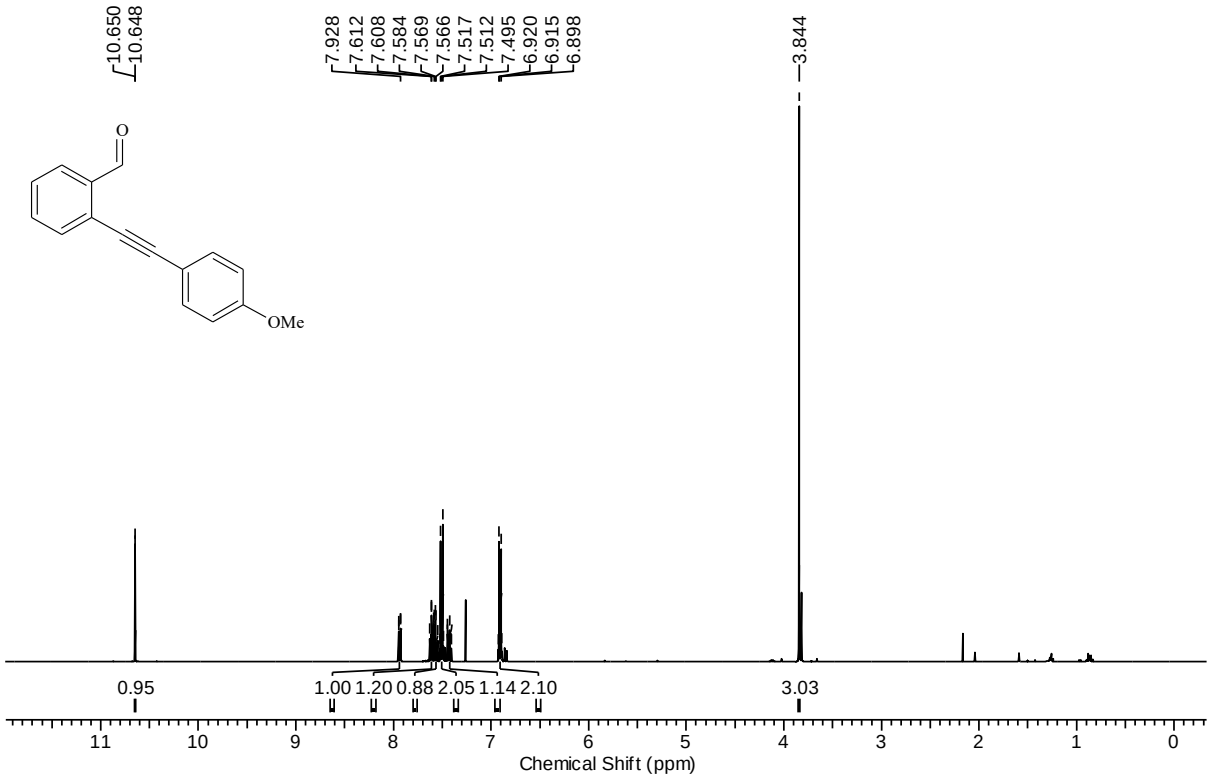


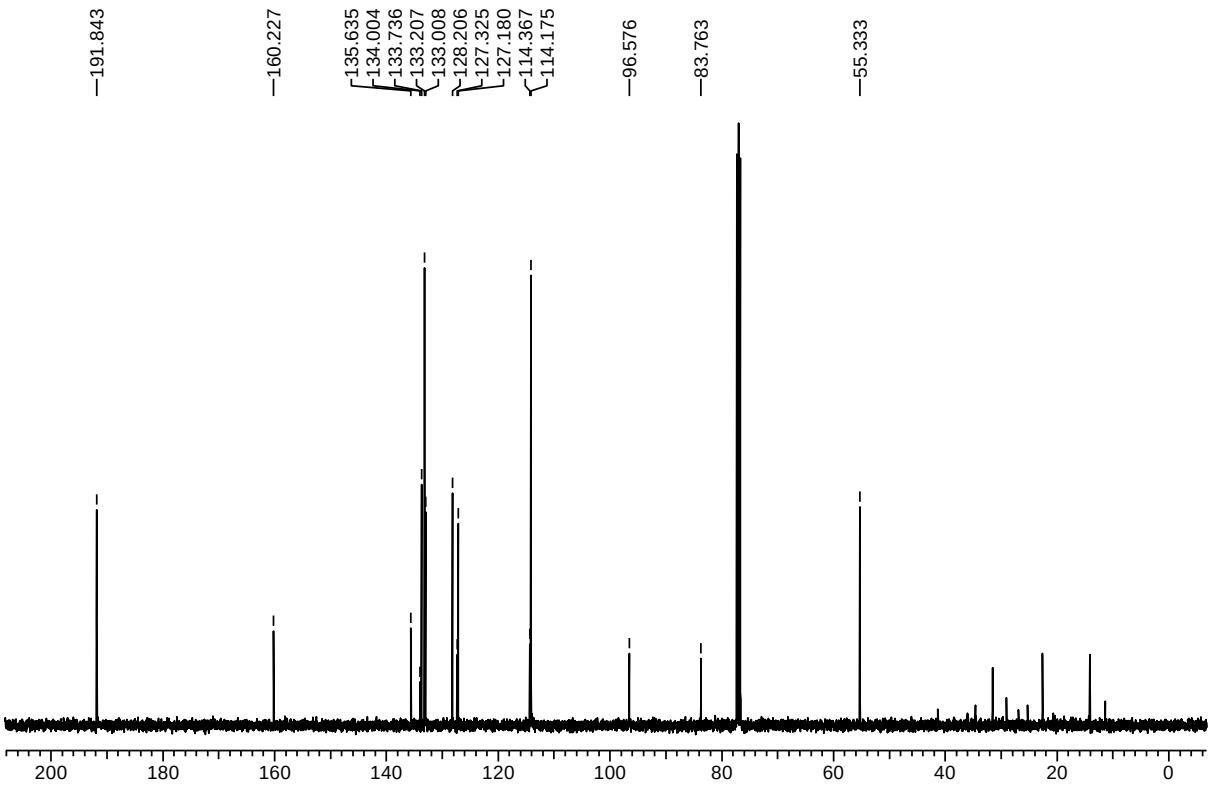
2-((4-(Trifluoromethyl)phenyl)ethynyl)benzaldehyde (S-1b)



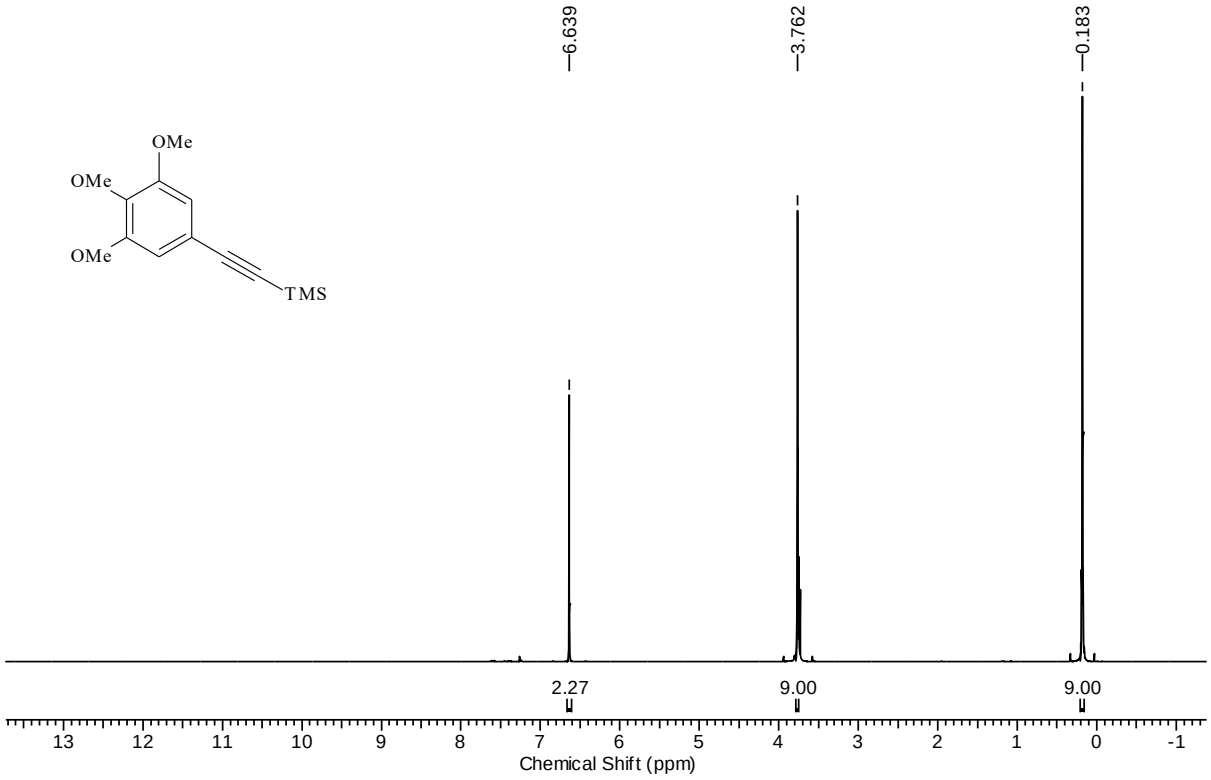


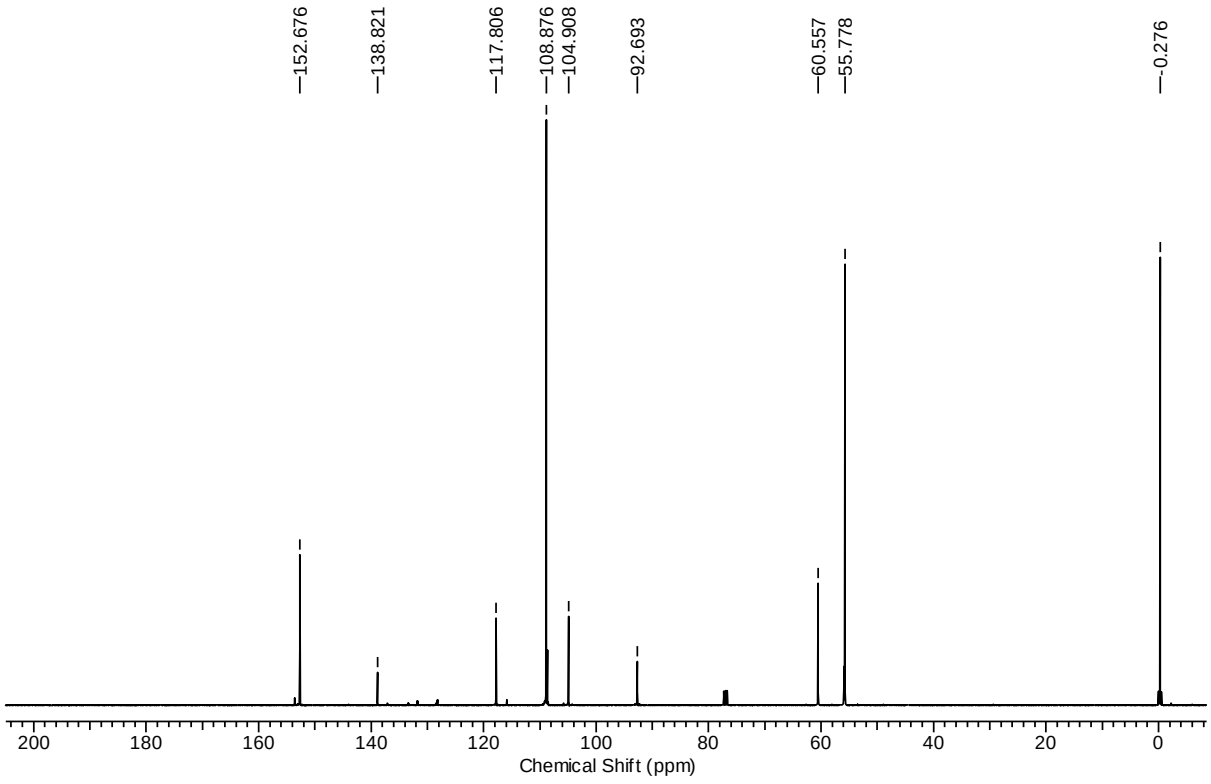
2-((4-Methoxyphenyl)ethynyl)benzaldehyde (S-1c)



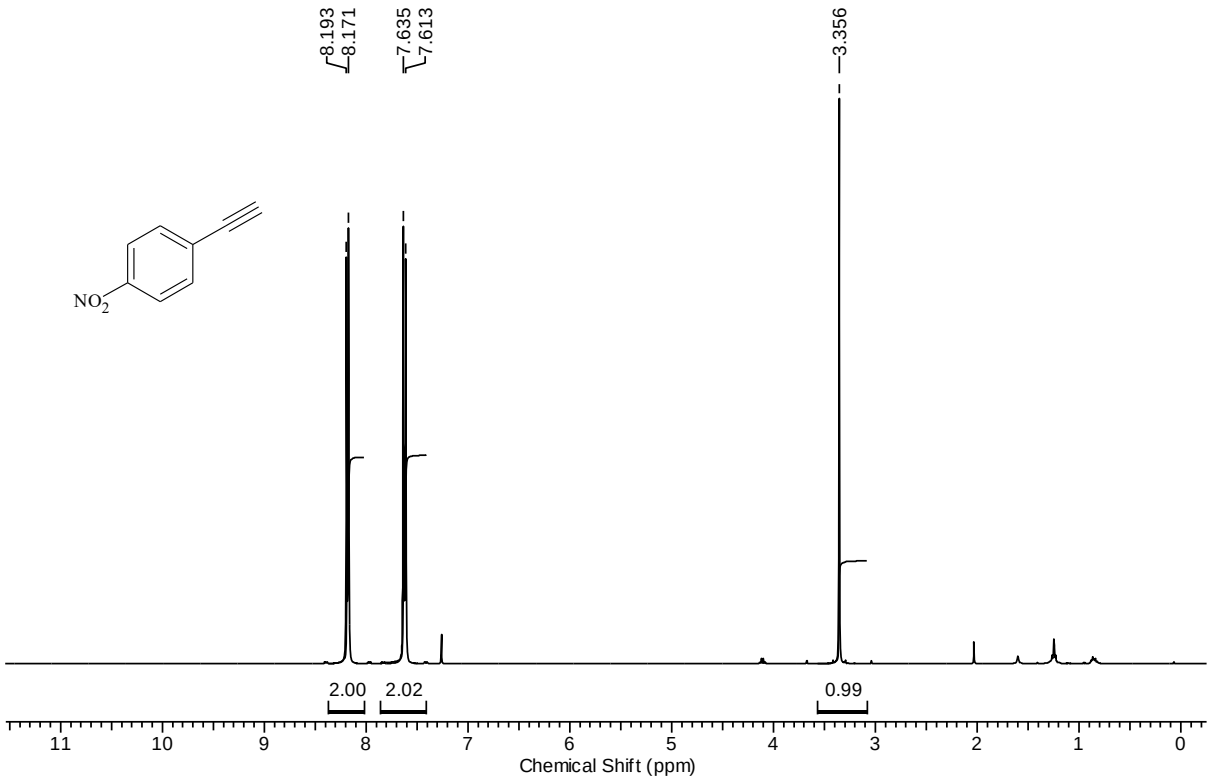


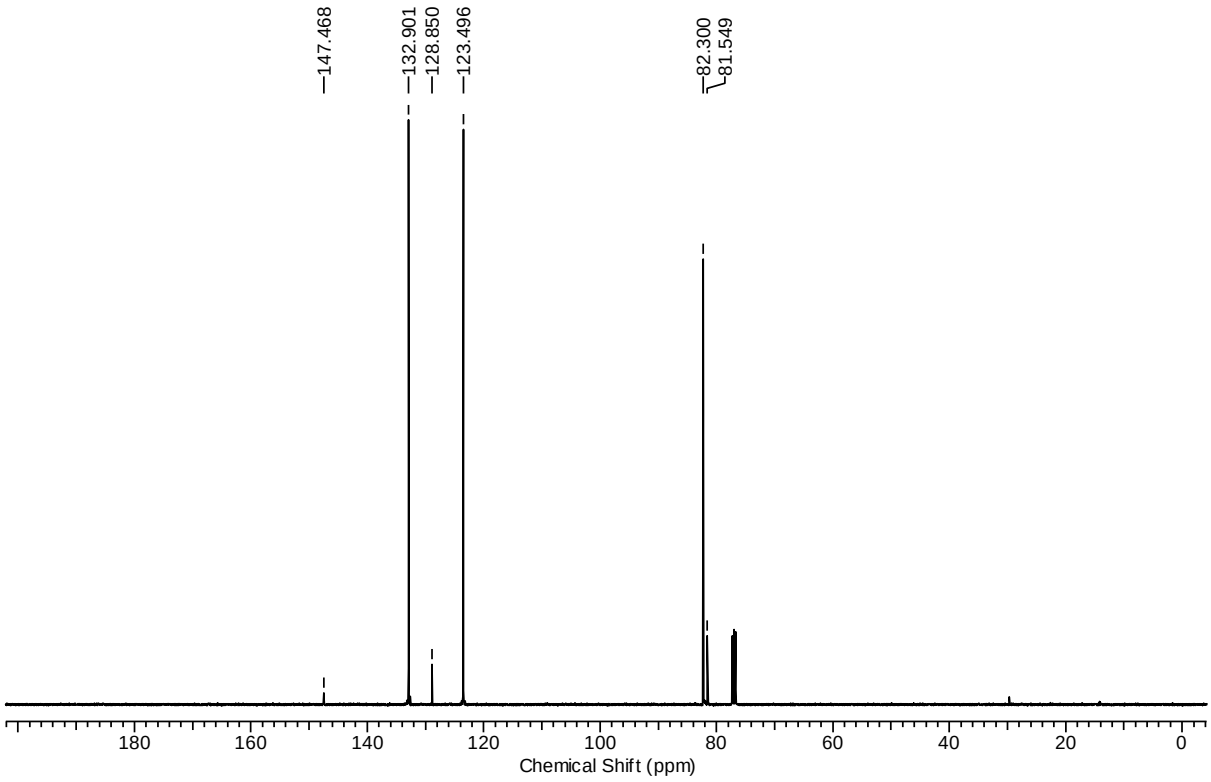
Trimethyl((3,4,5-trimethoxyphenyl)ethynyl)silane (S-2a)



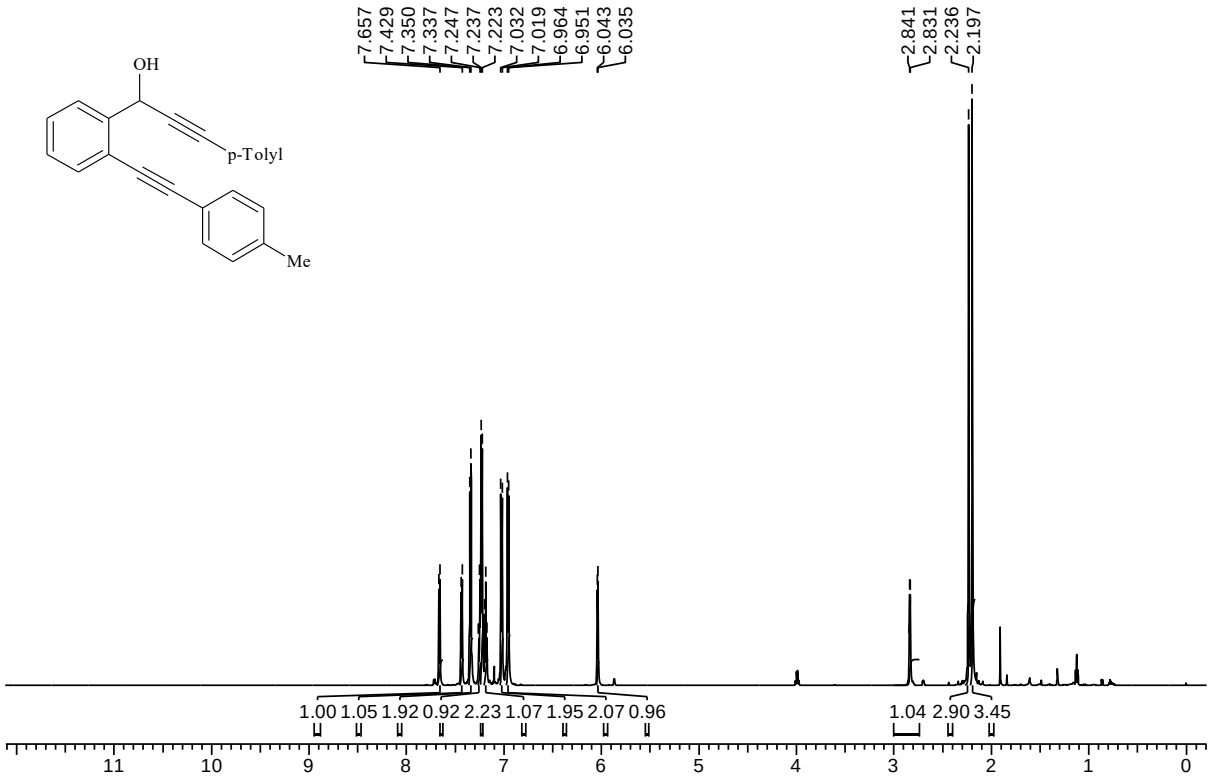


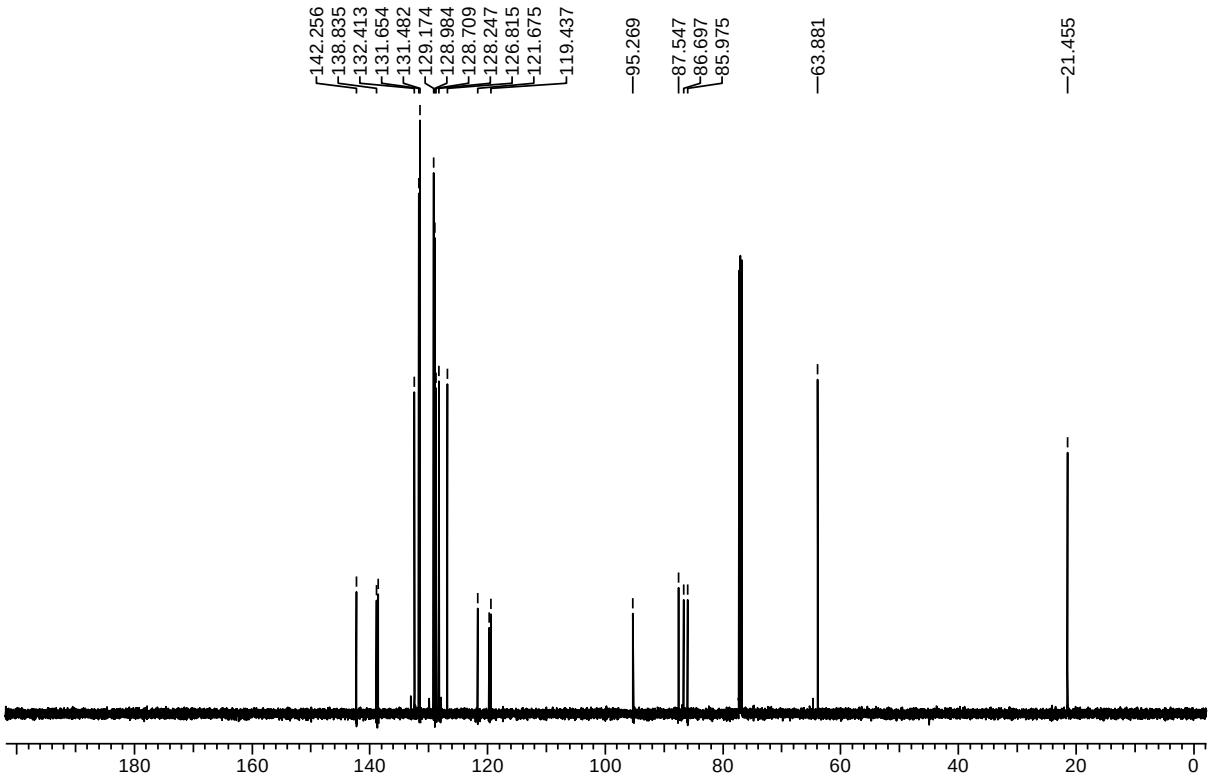
1-Ethynyl-4-nitrobenzene (S-2b)



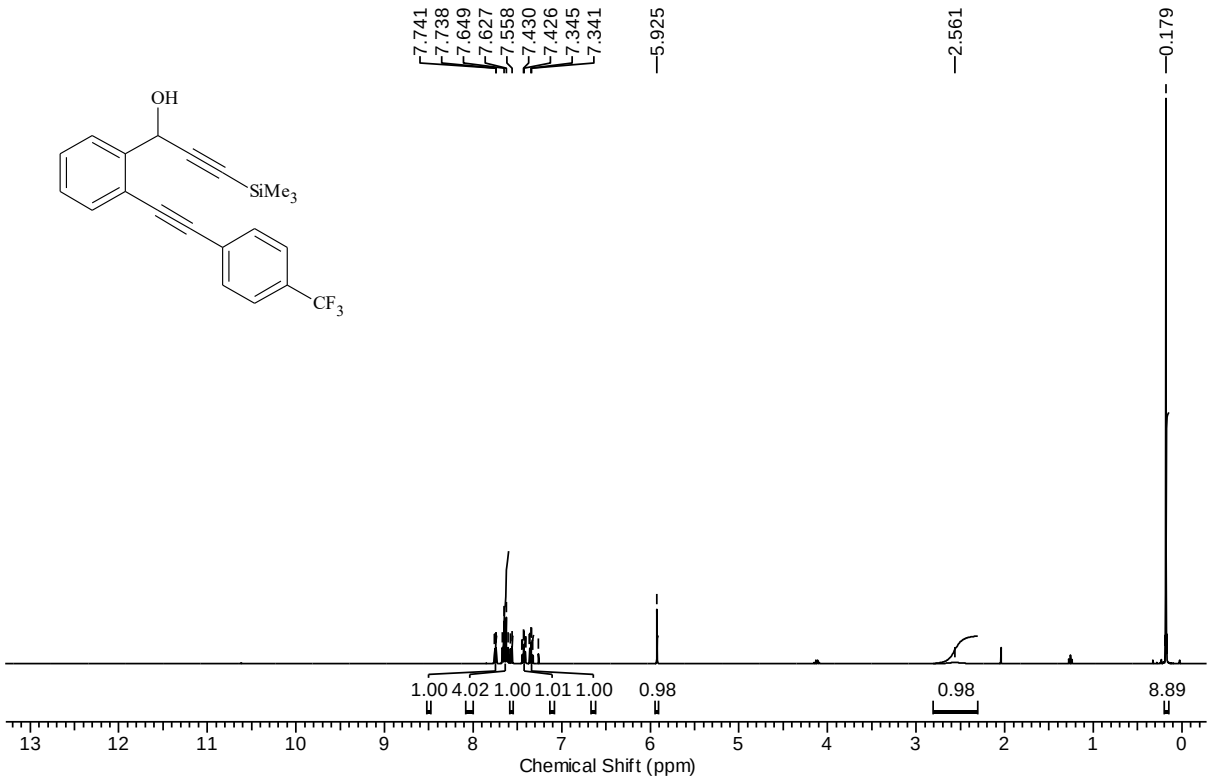


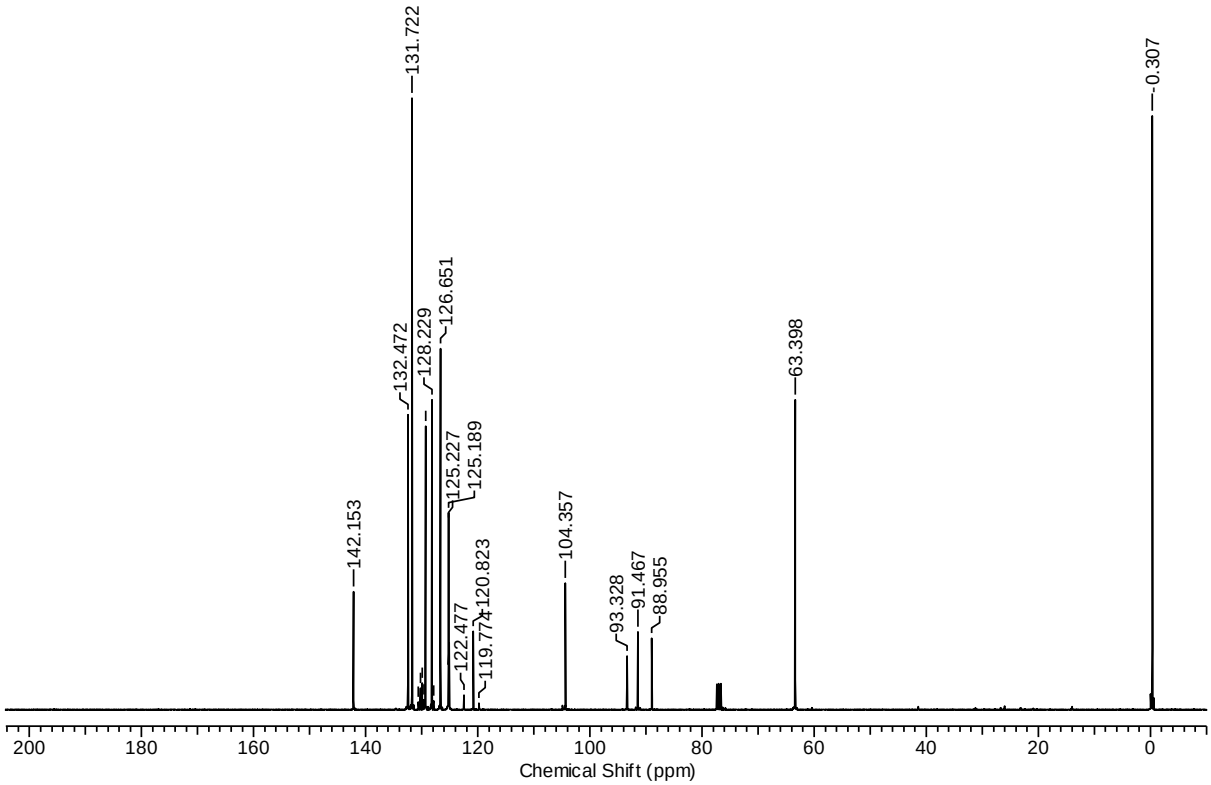
3-(*p*-Tolyl)-1-(2-(*p*-tolylethynyl)phenyl)prop-2-yn-1-ol (1c)



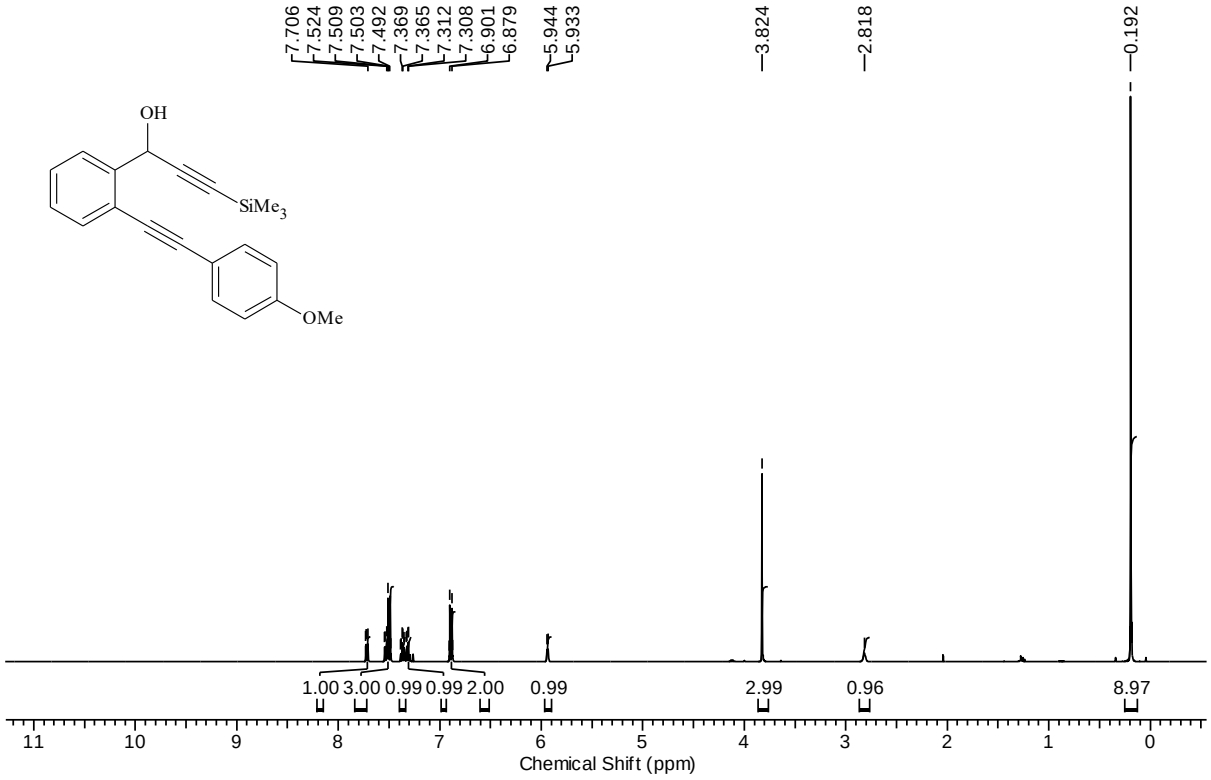


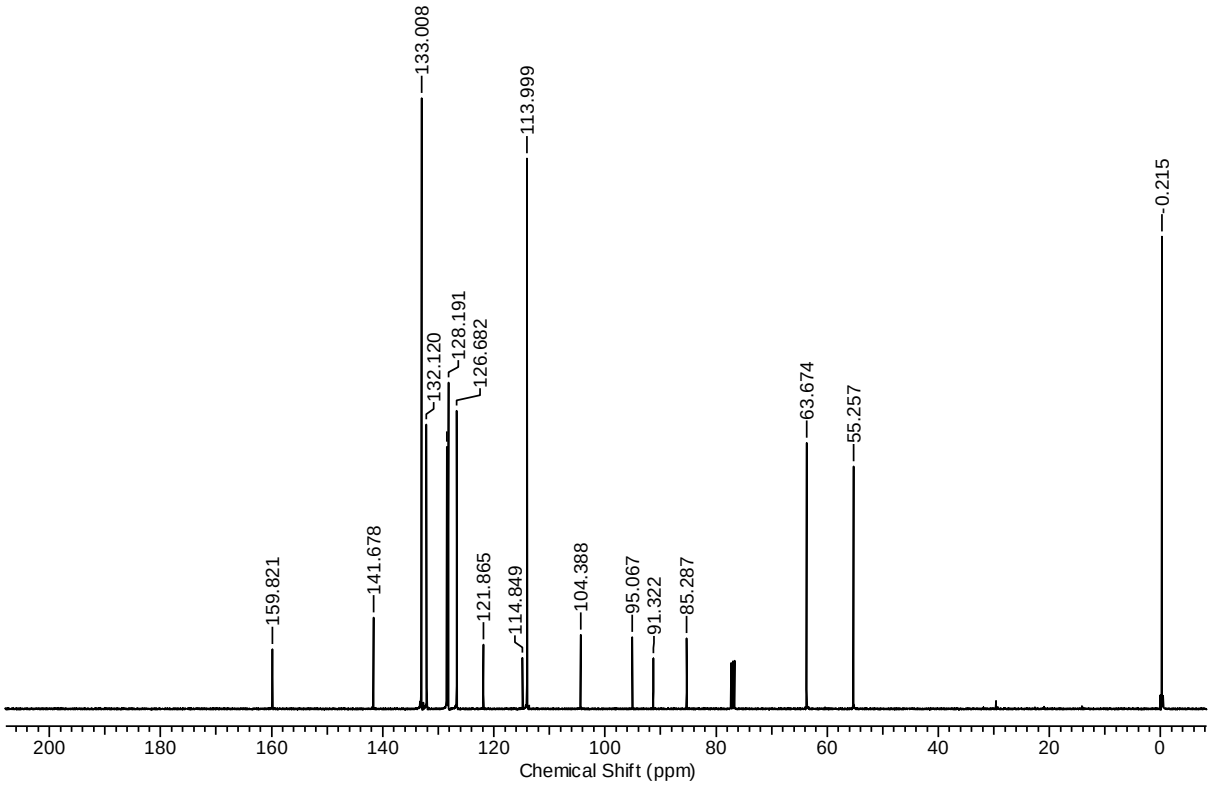
1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S-3a)



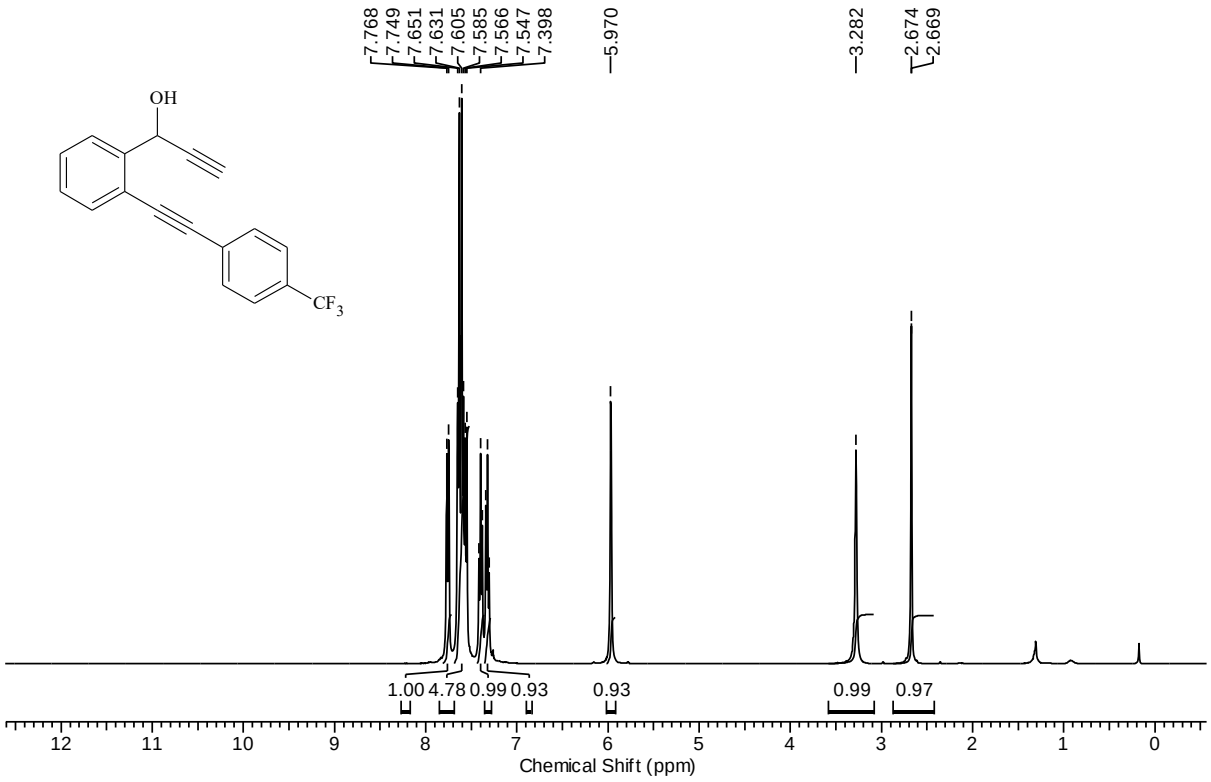


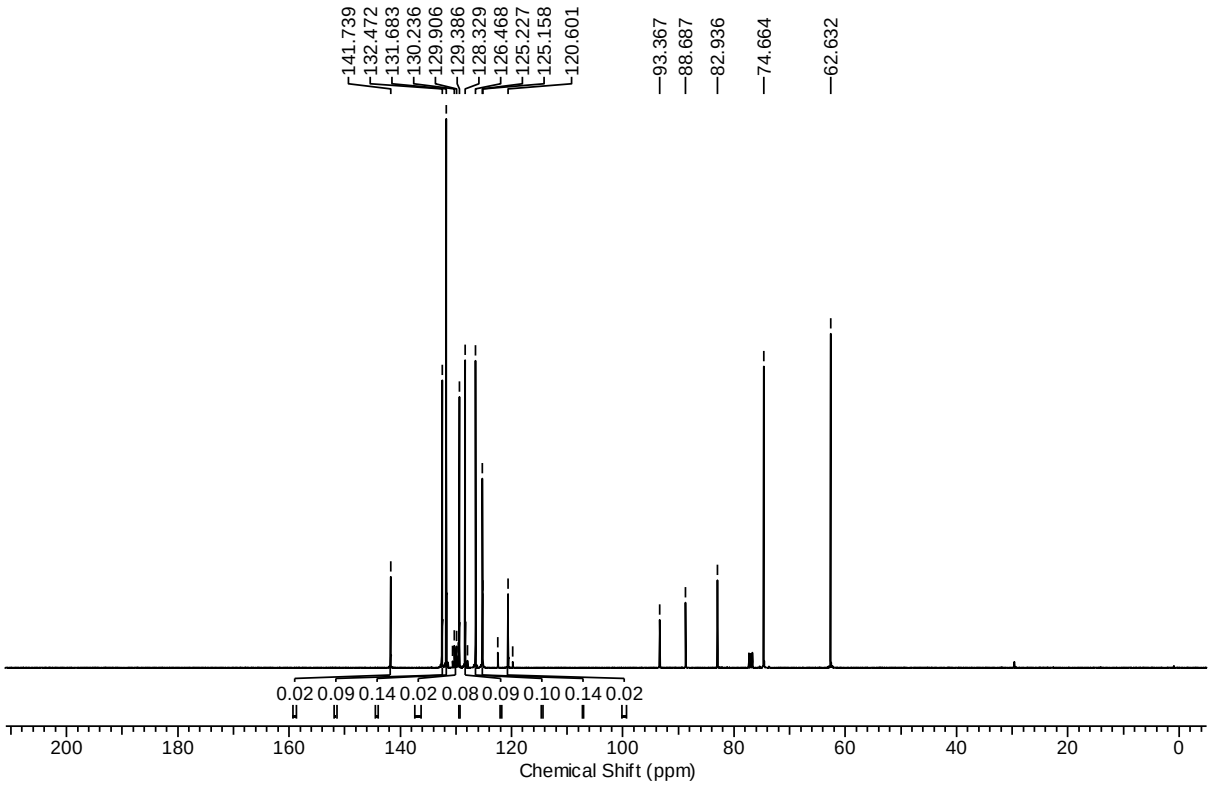
1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S-3b)



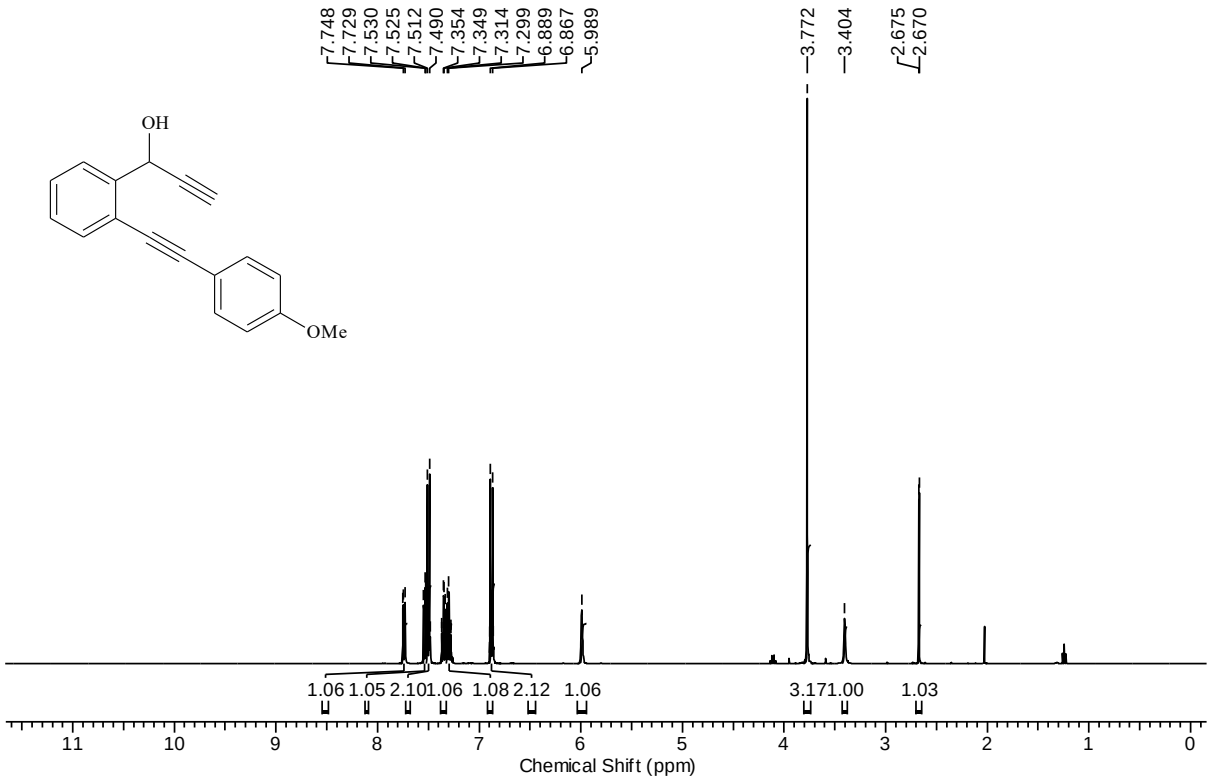


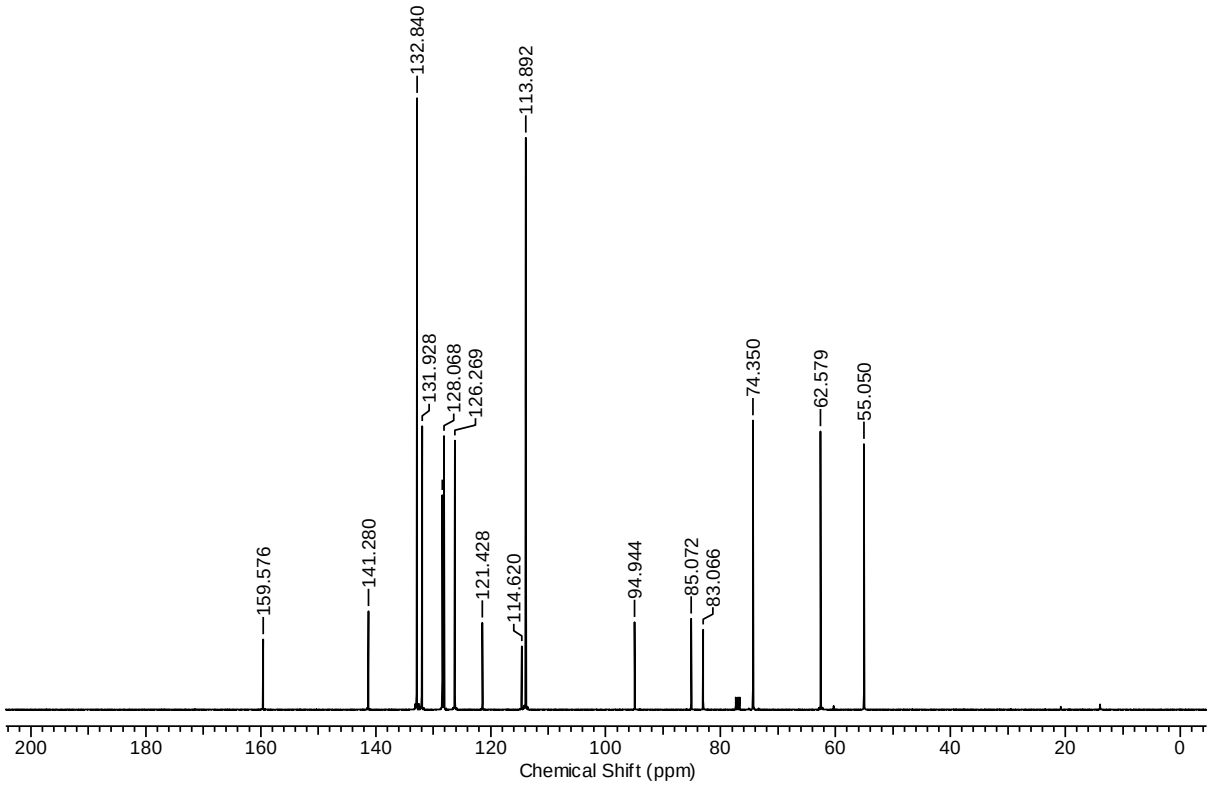
1-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)prop-2-yn-1-ol (5a)



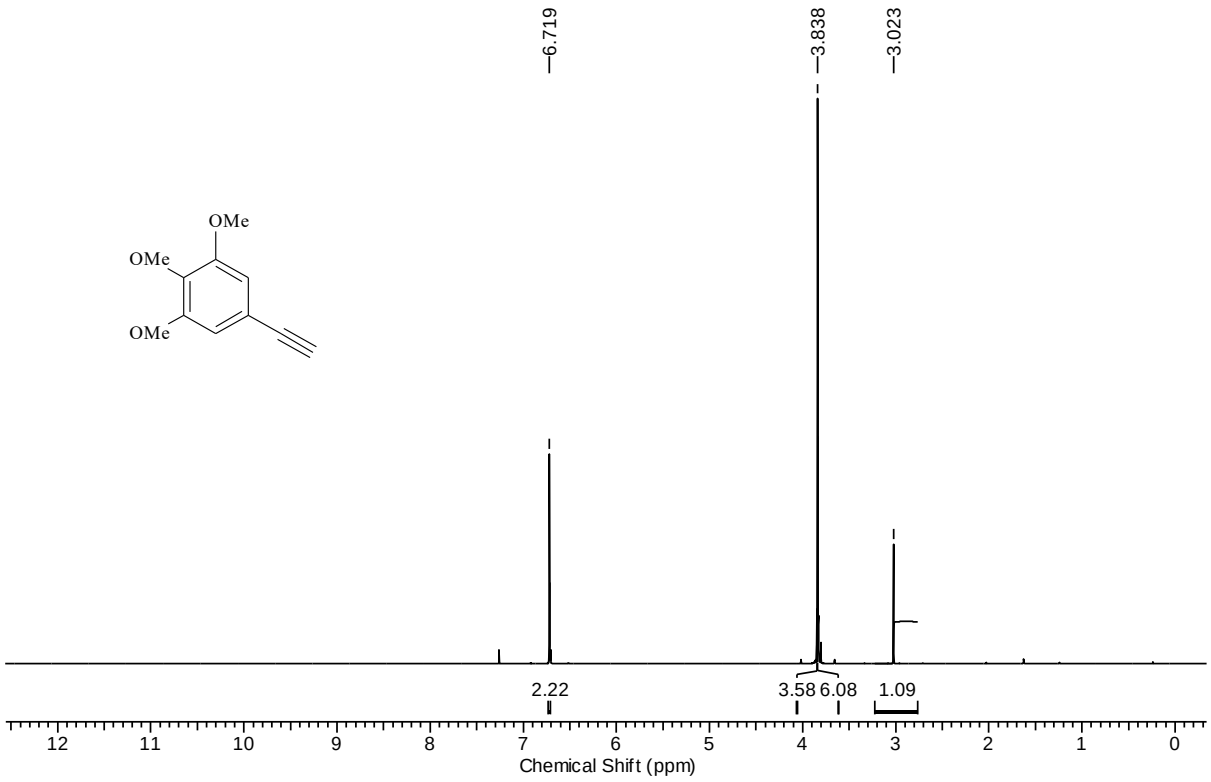


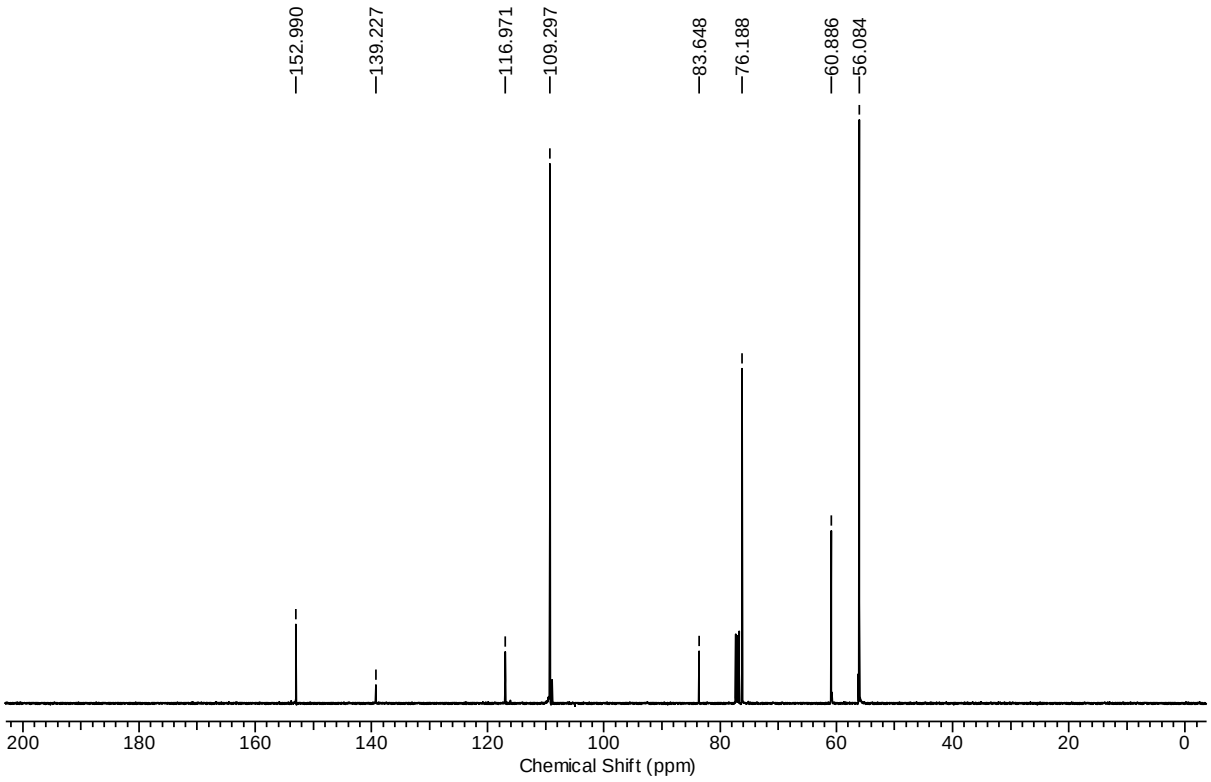
1-(2-((4-Methoxyphenyl)ethynyl)phenyl)prop-2-yn-1-ol (5b)



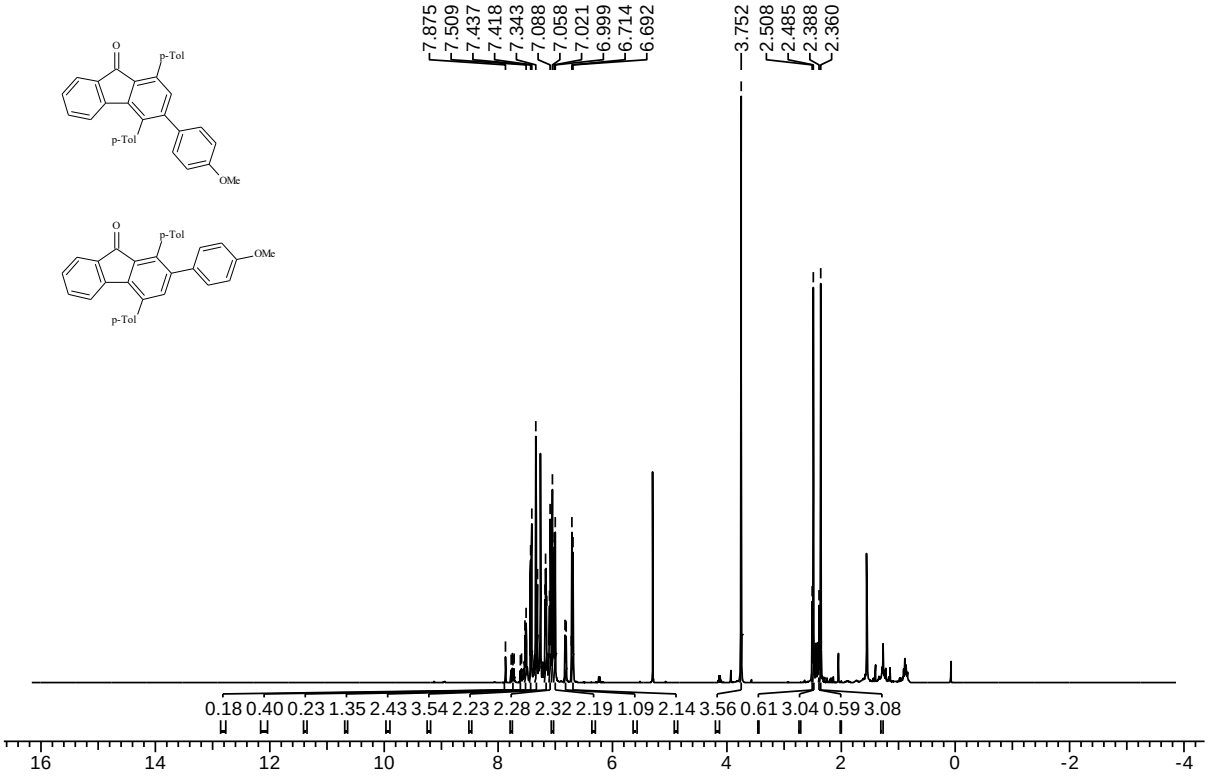


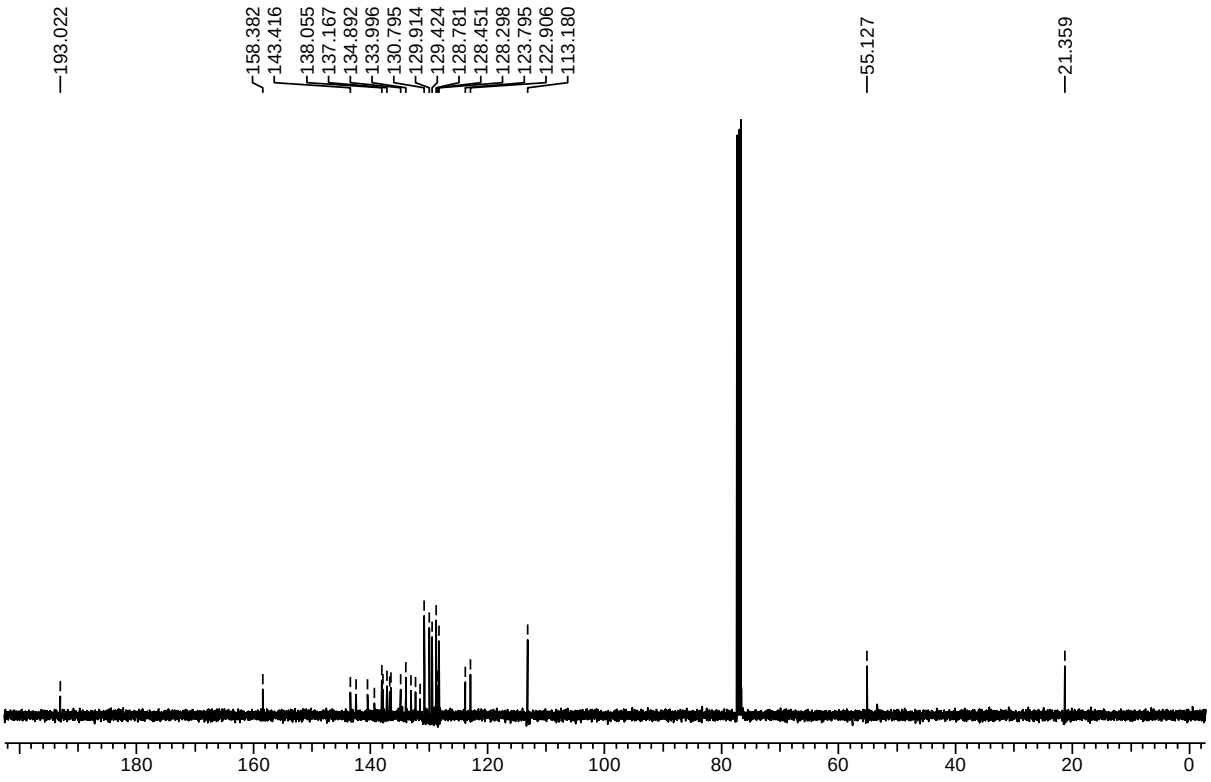
5-Ethynyl-1,2,3-trimethoxybenzene (S-4)



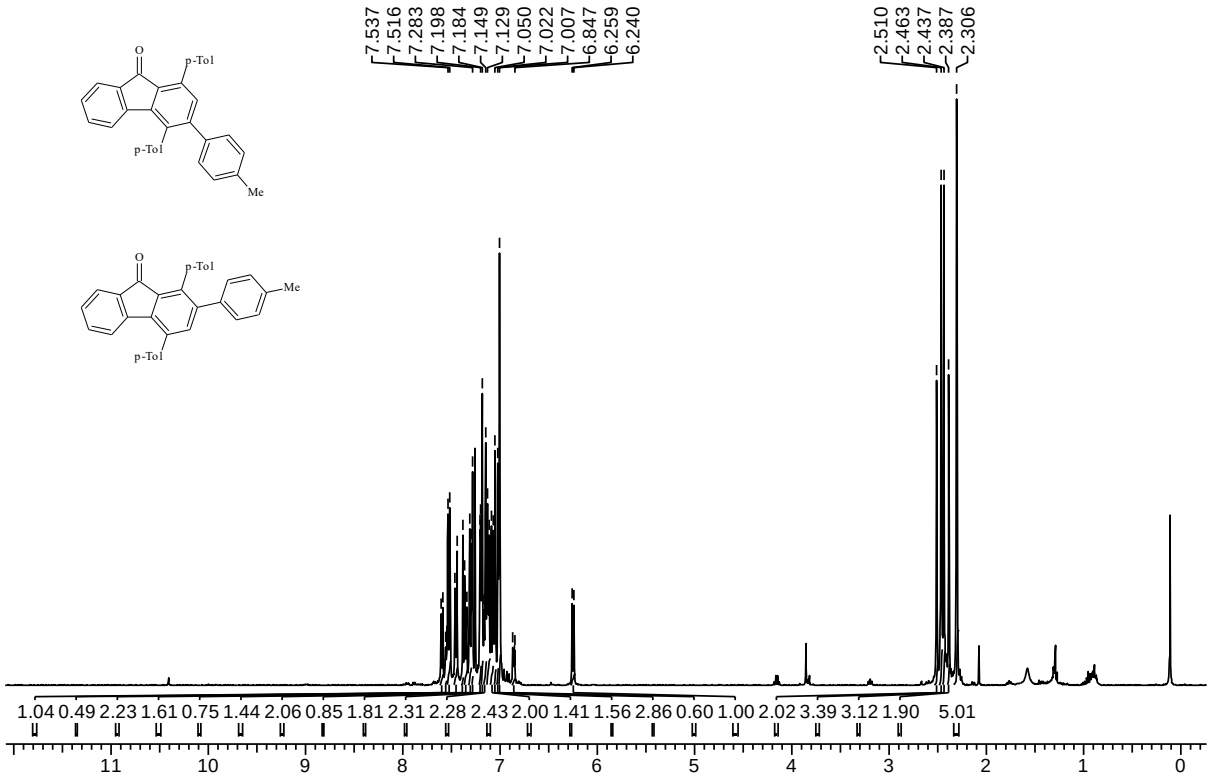


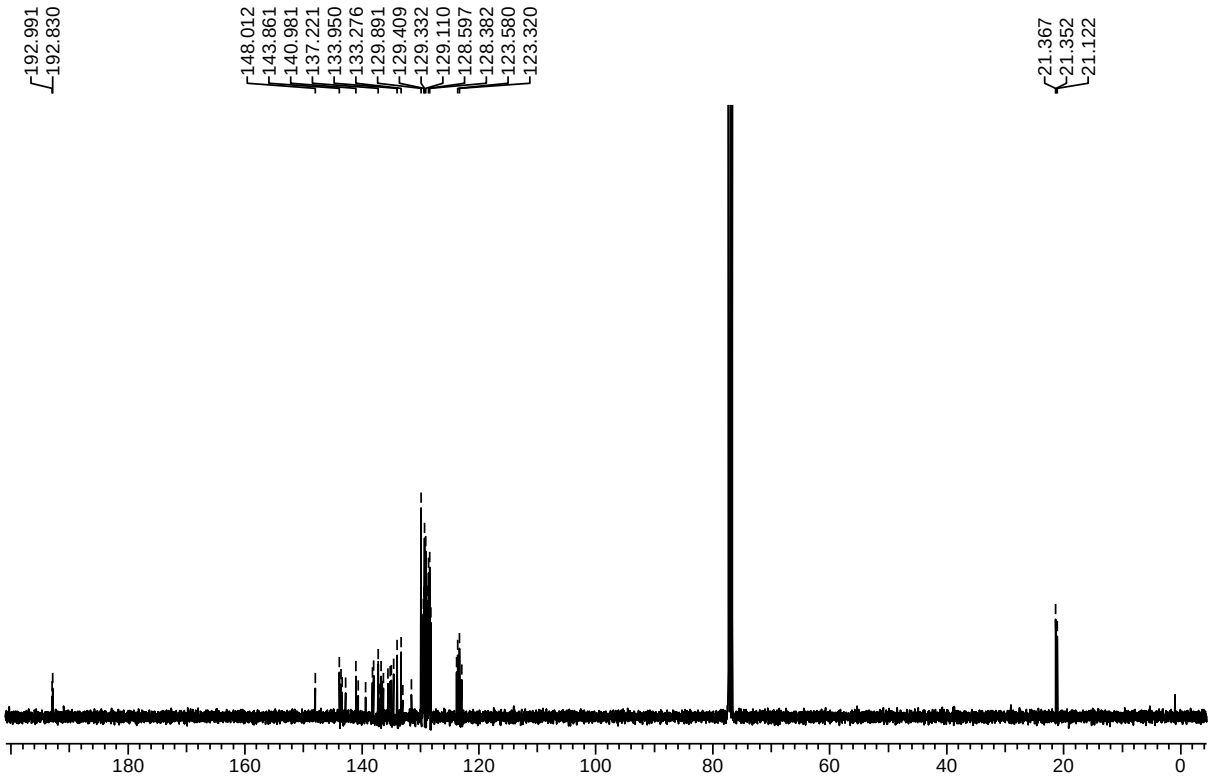
2-(4-Methoxyphenyl)-1,4-bi(s*p*-tolyl)-9*H*-fluoren-9-one (4a) and 3-(4-methoxyphenyl) -1,4-di(*p*-tolyl)-9*H*-fluoren-9-one (4'a)



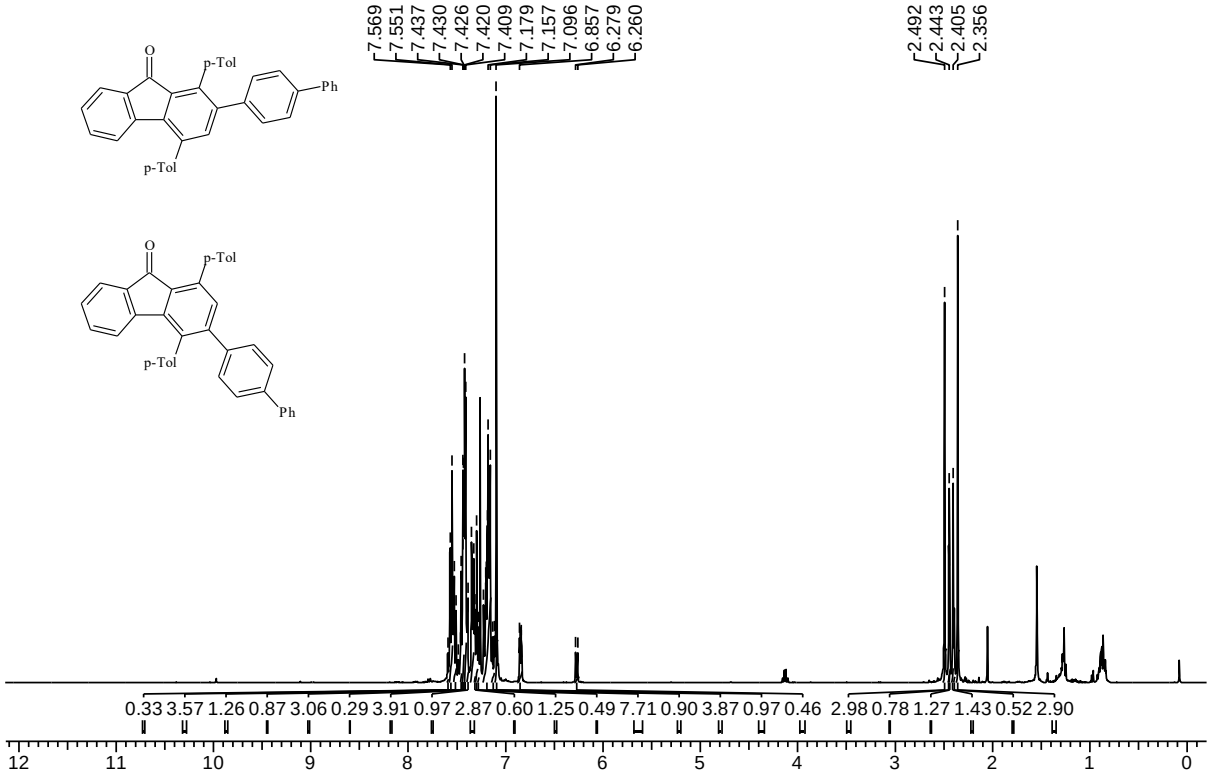


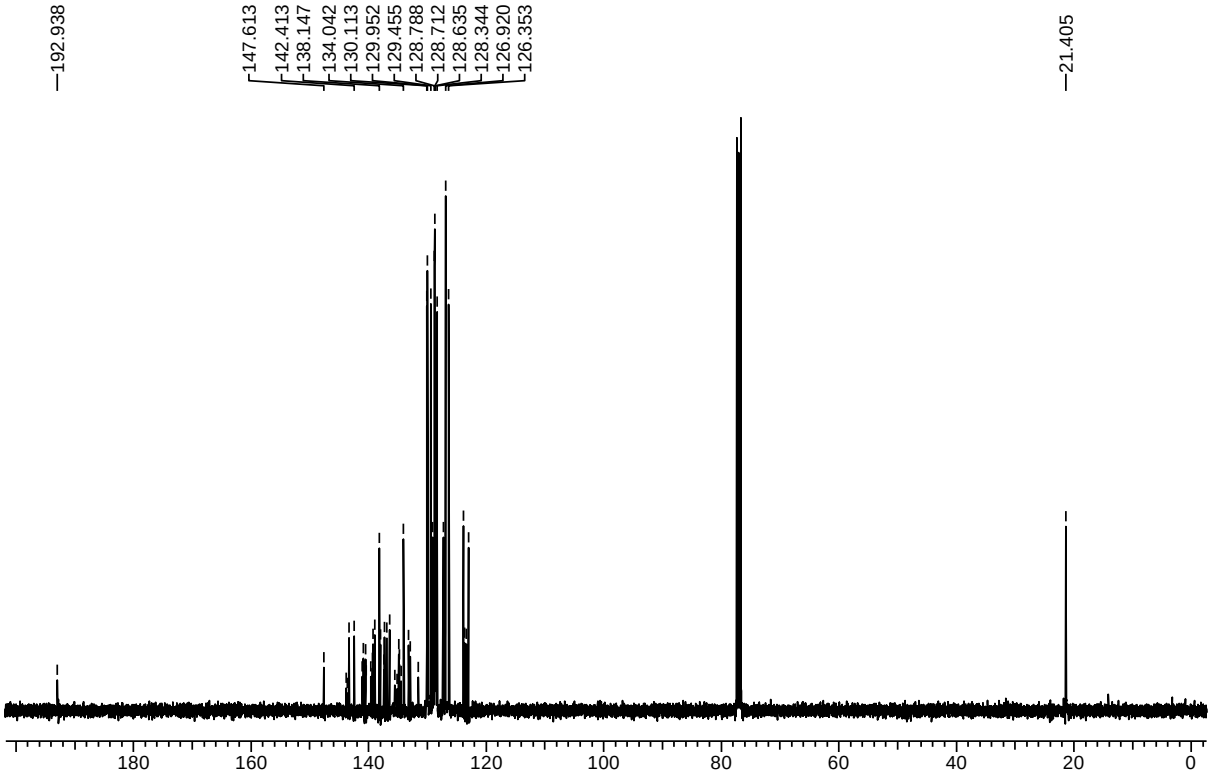
1,2,4-Tris(*p*-tolyl)-9*H*-fluoren-9-one (4b) and 1,3,4-tris(*p*-tolyl)-9*H*-fluoren-9-one (4'b)



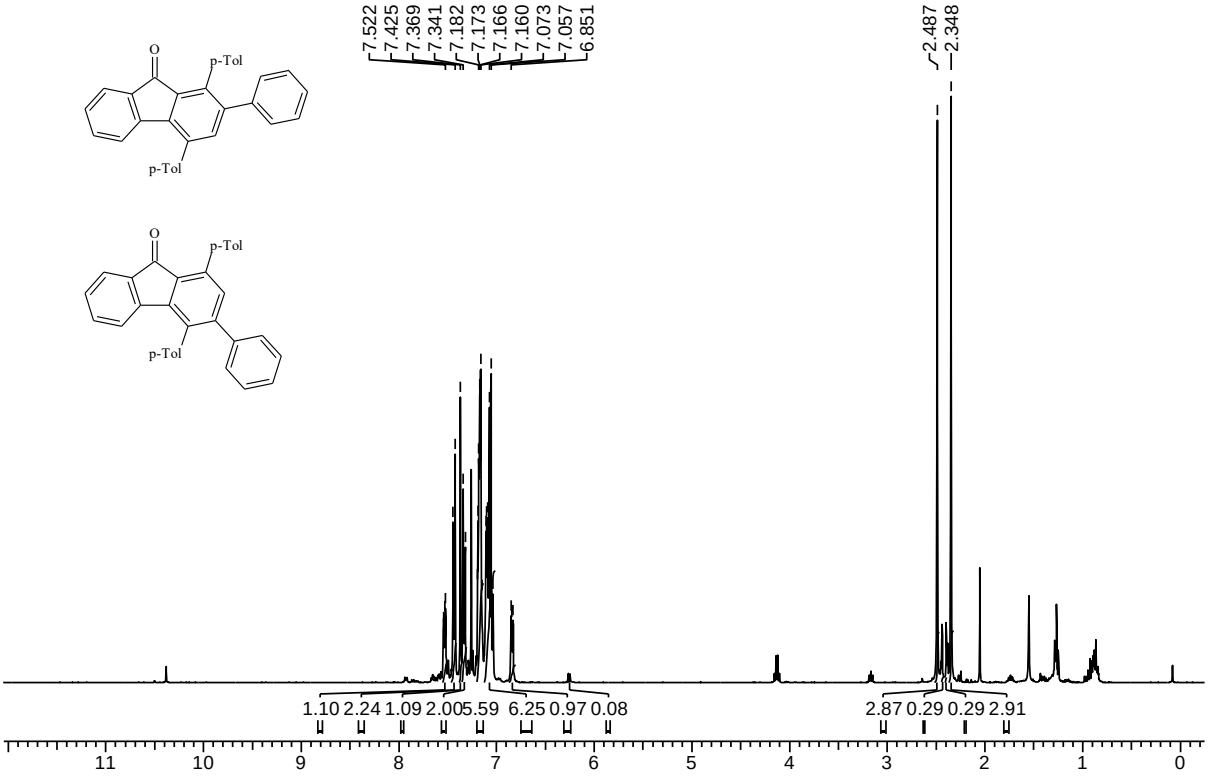


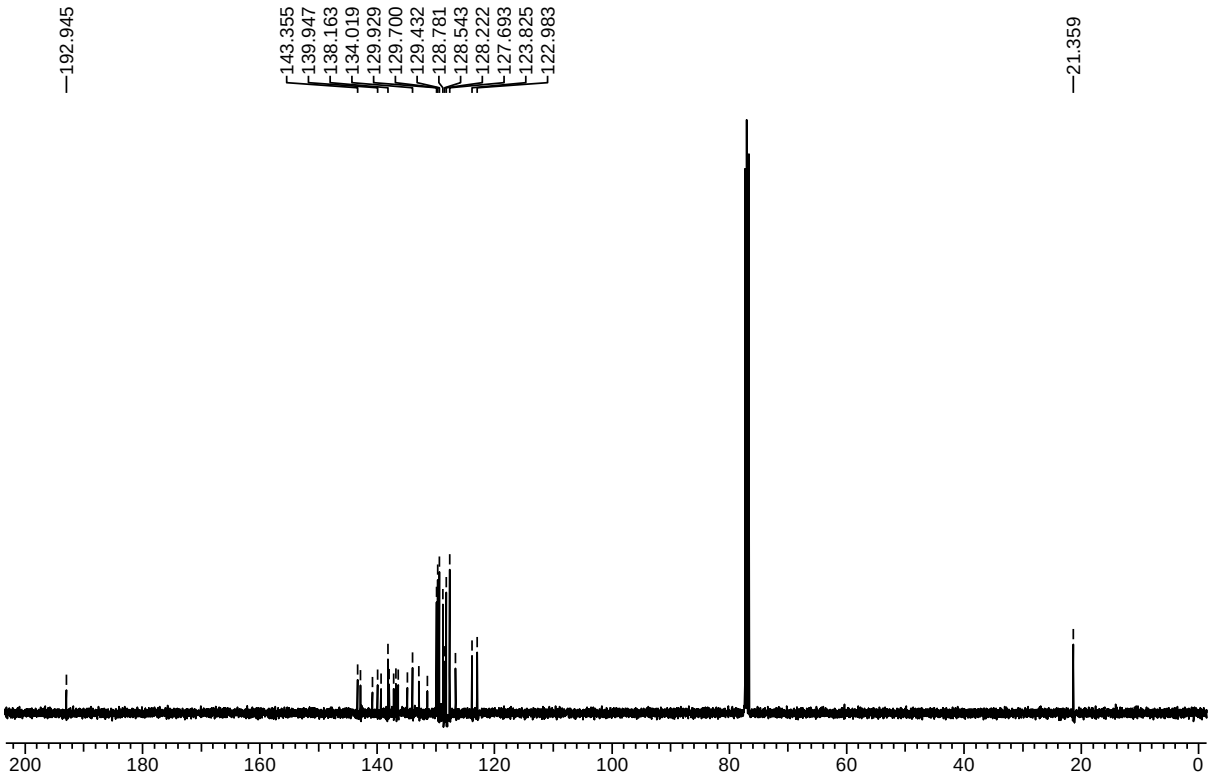
2-([1,1'-Biphenyl]-4-yl)-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4c) and 3-([1,1'-biphenyl]-4-yl)-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4'c)



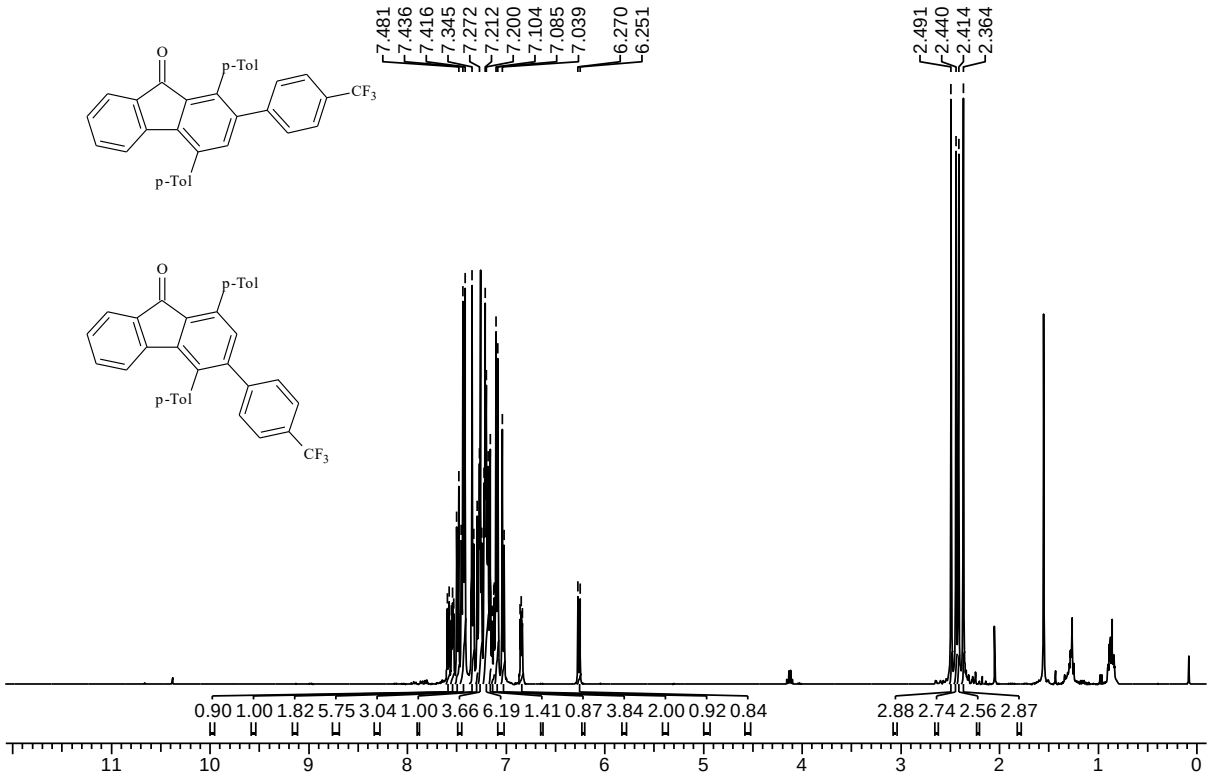


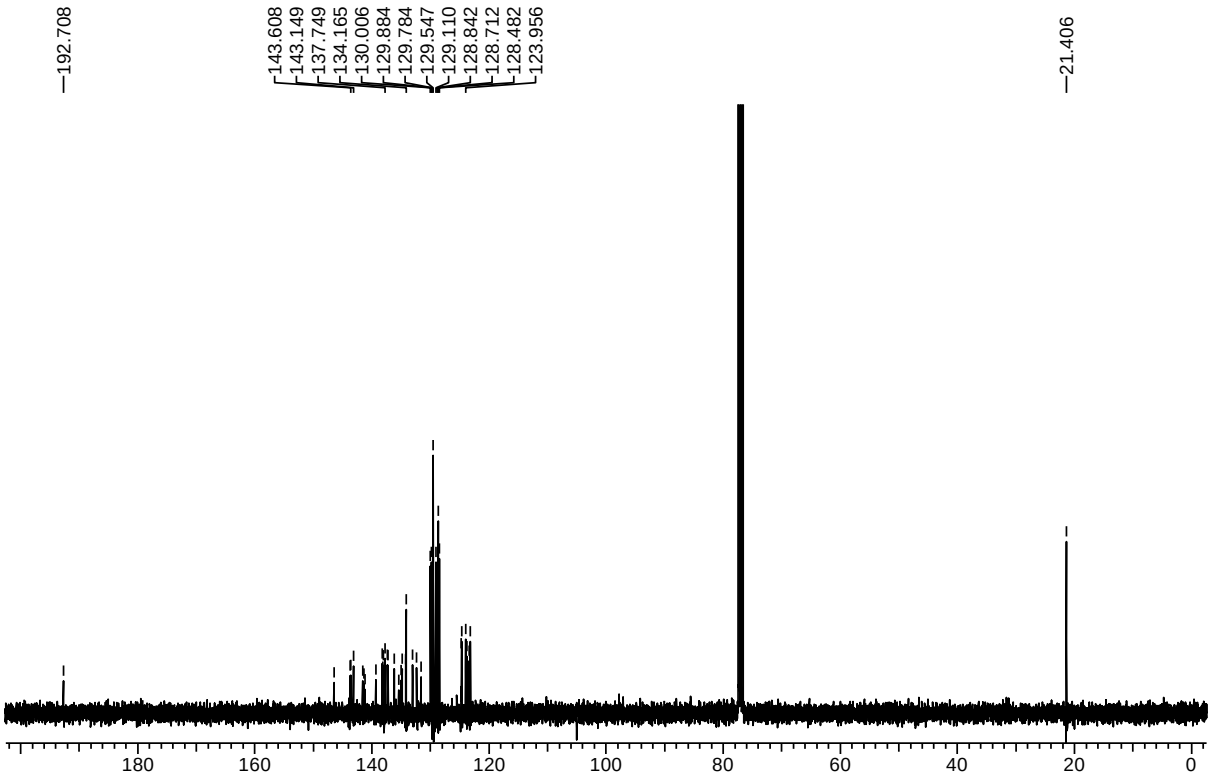
2-Phenyl-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4d) and 3-phenyl-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4'd)



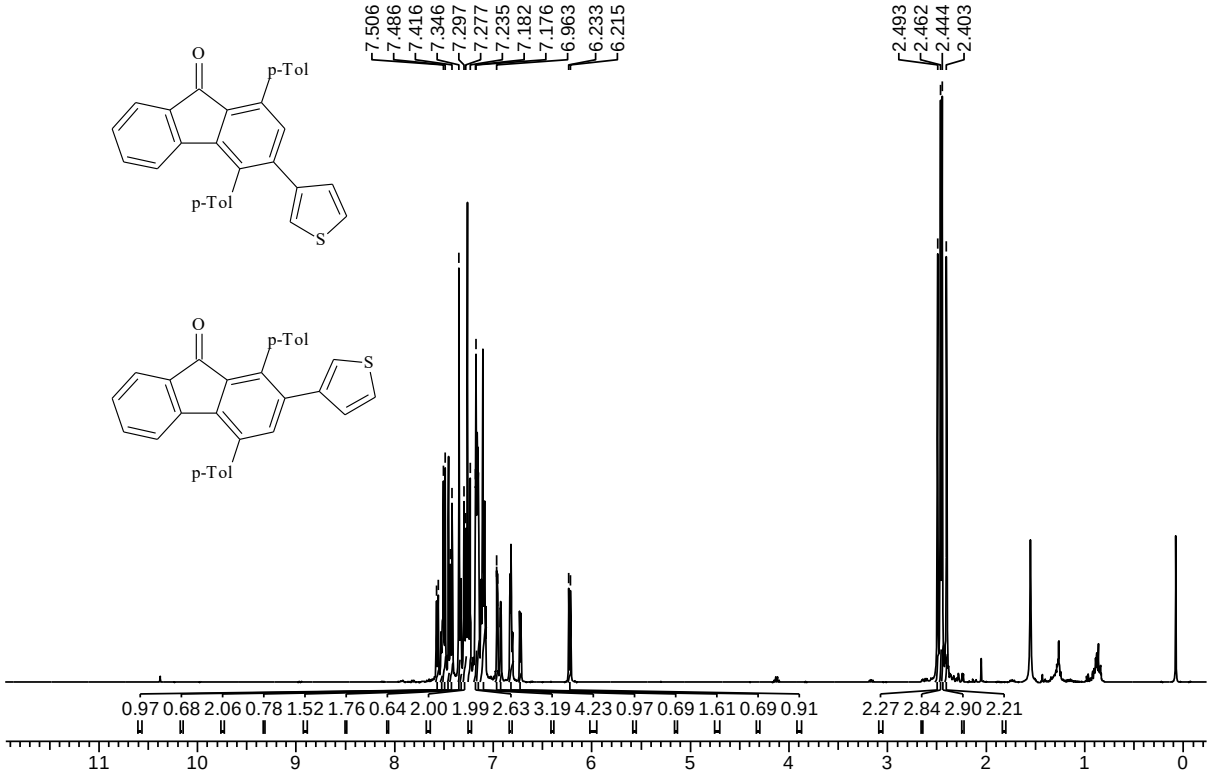


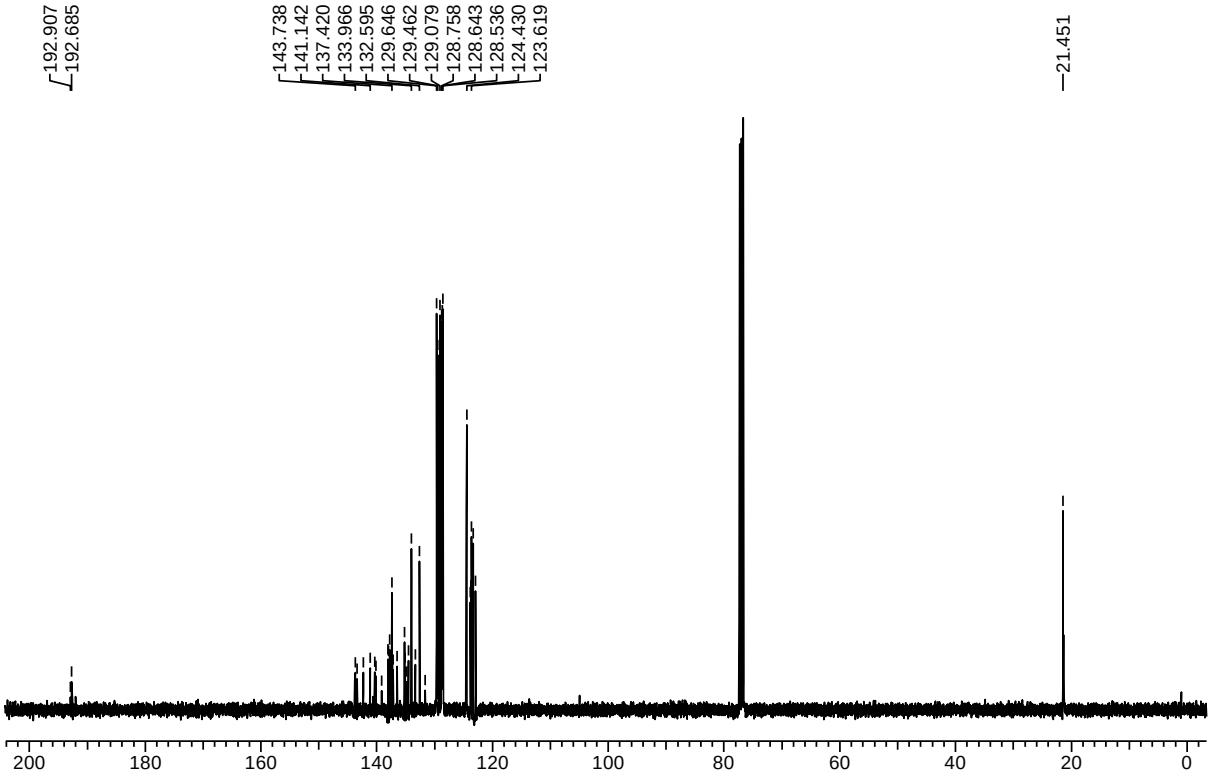
1,4-Bis(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (4e) and 1,4-bis(*p*-tolyl)-3-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (4'e)



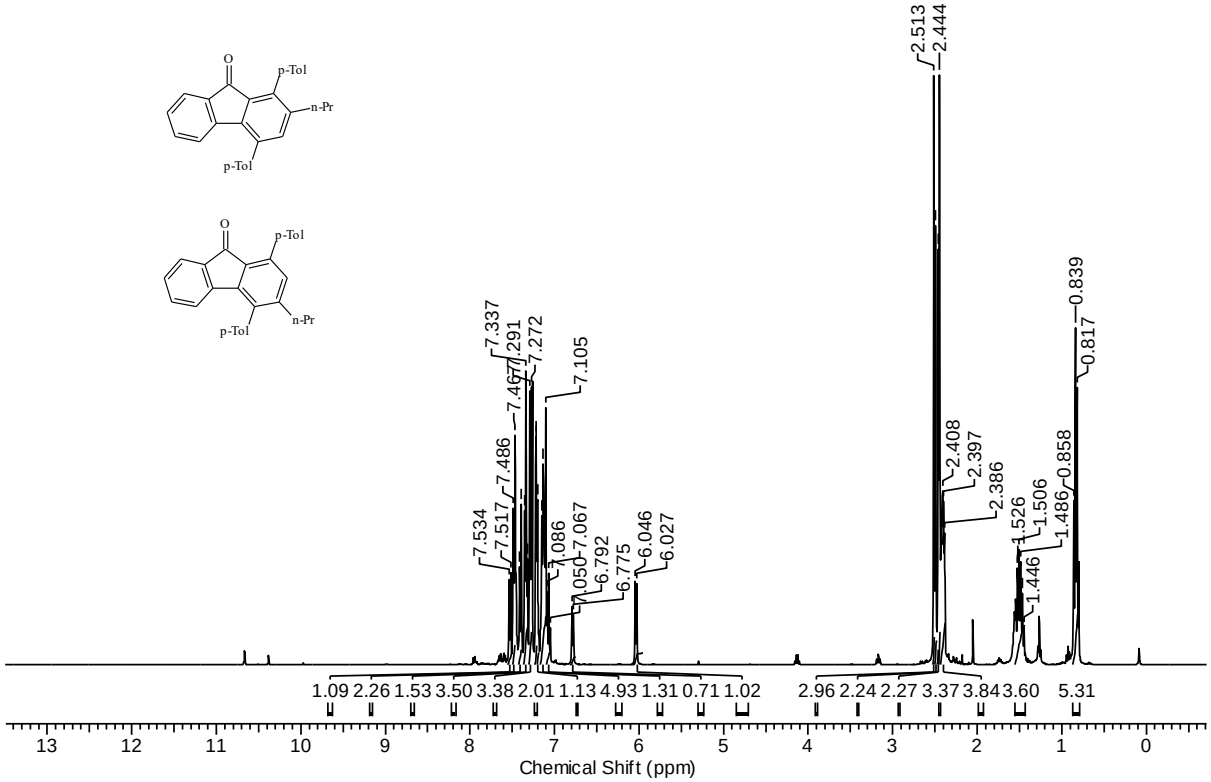


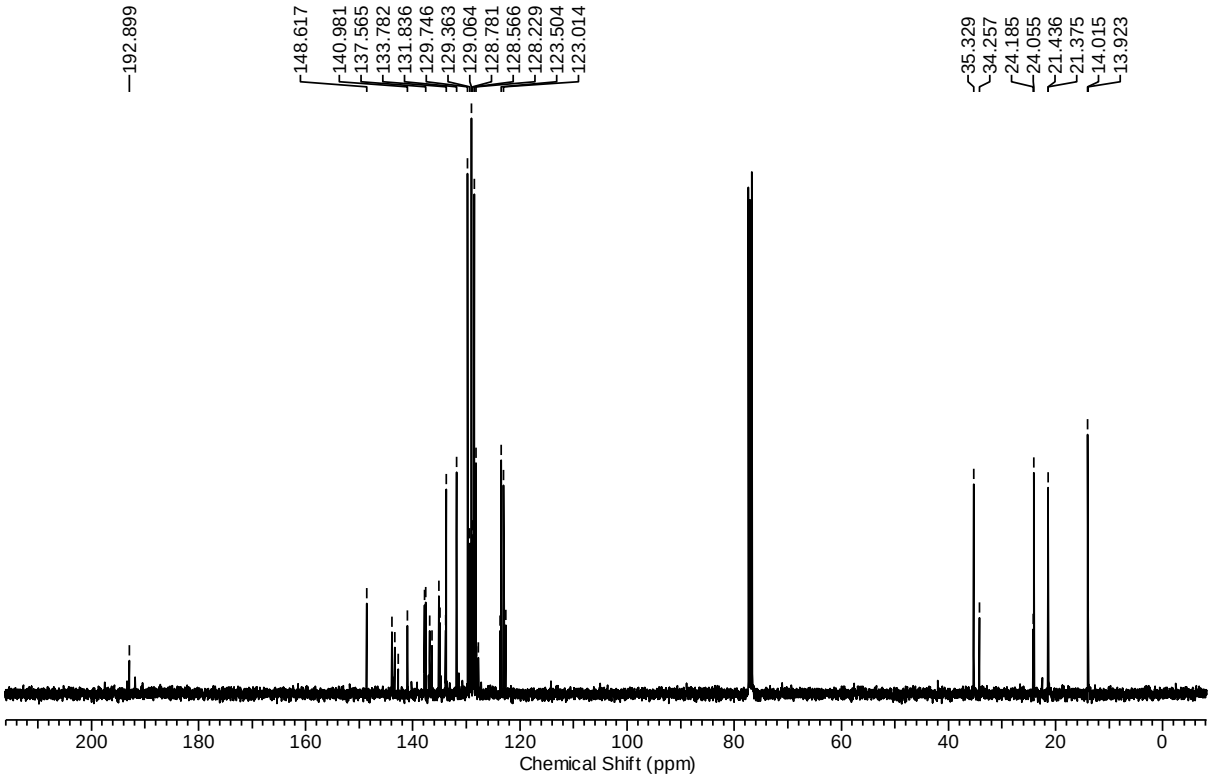
2-(Thien-3-yl)-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4f) and 3-(thien-3-yl)-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4'f)



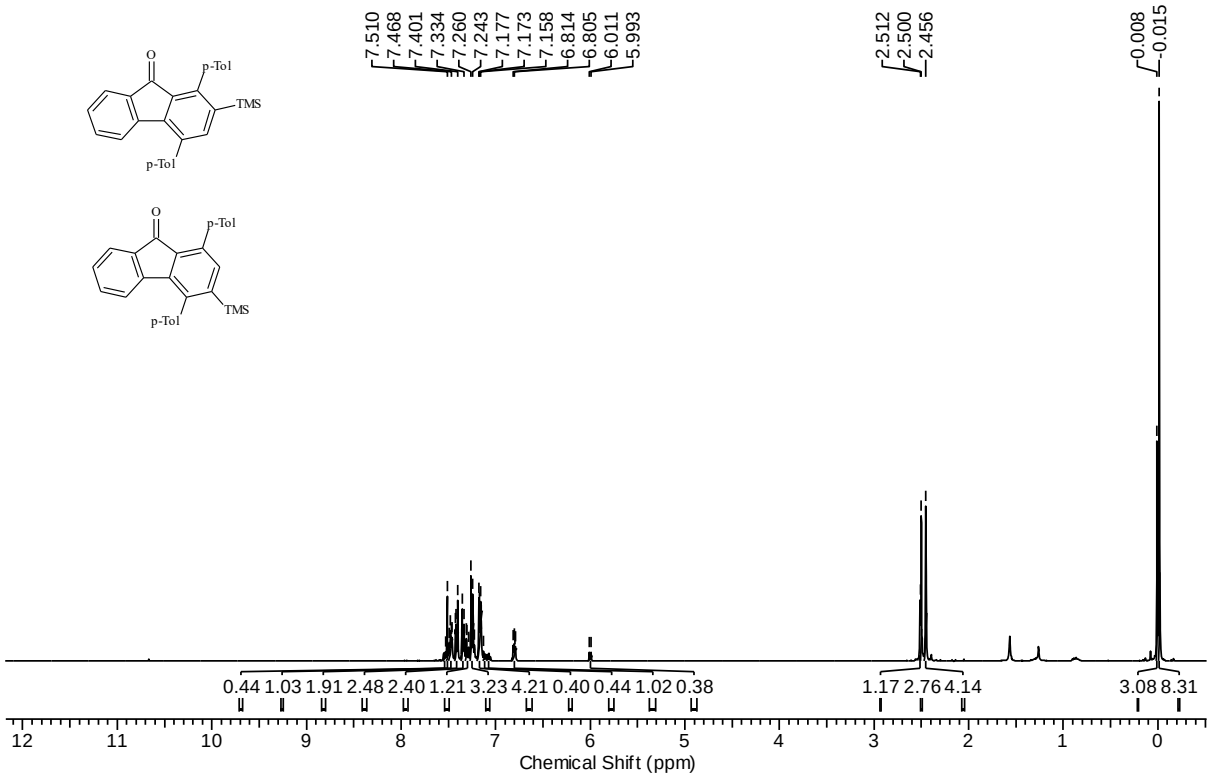


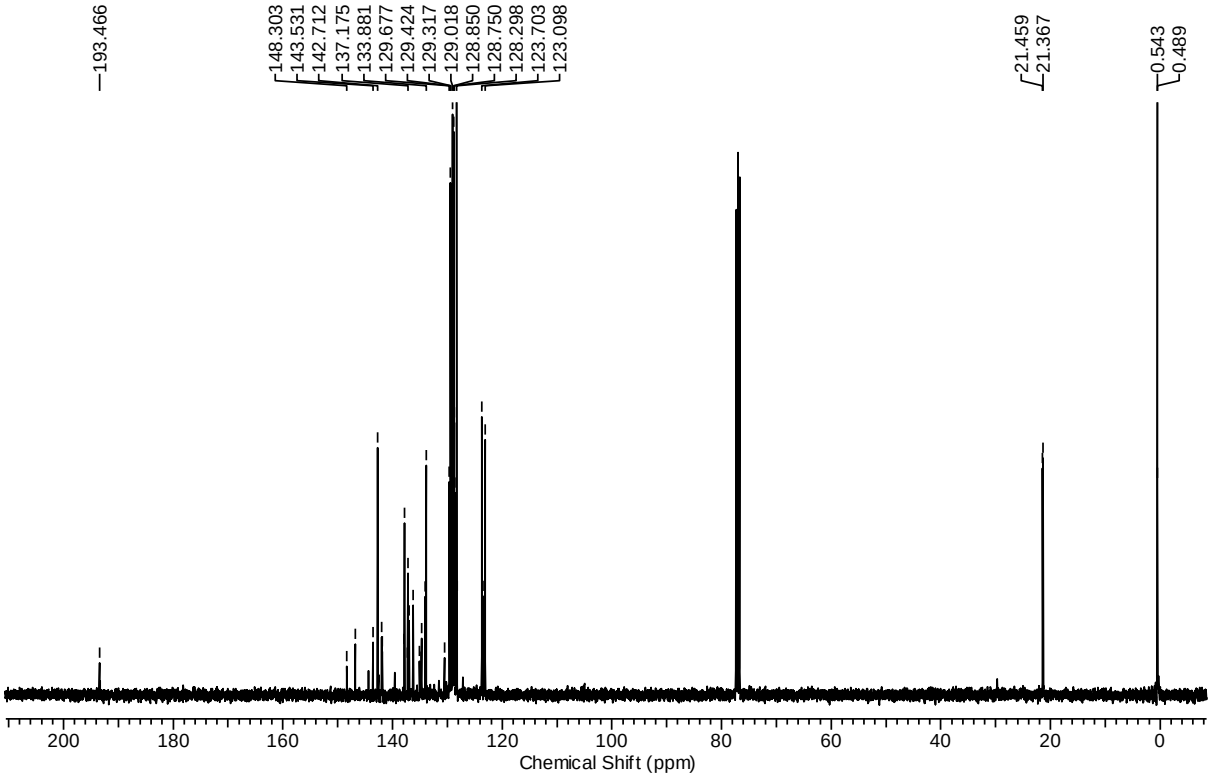
2-Propyl-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4g) and 3-propyl-1,4-bis(*p*-tolyl)-9*H*-fluoren-9-one (4’g)



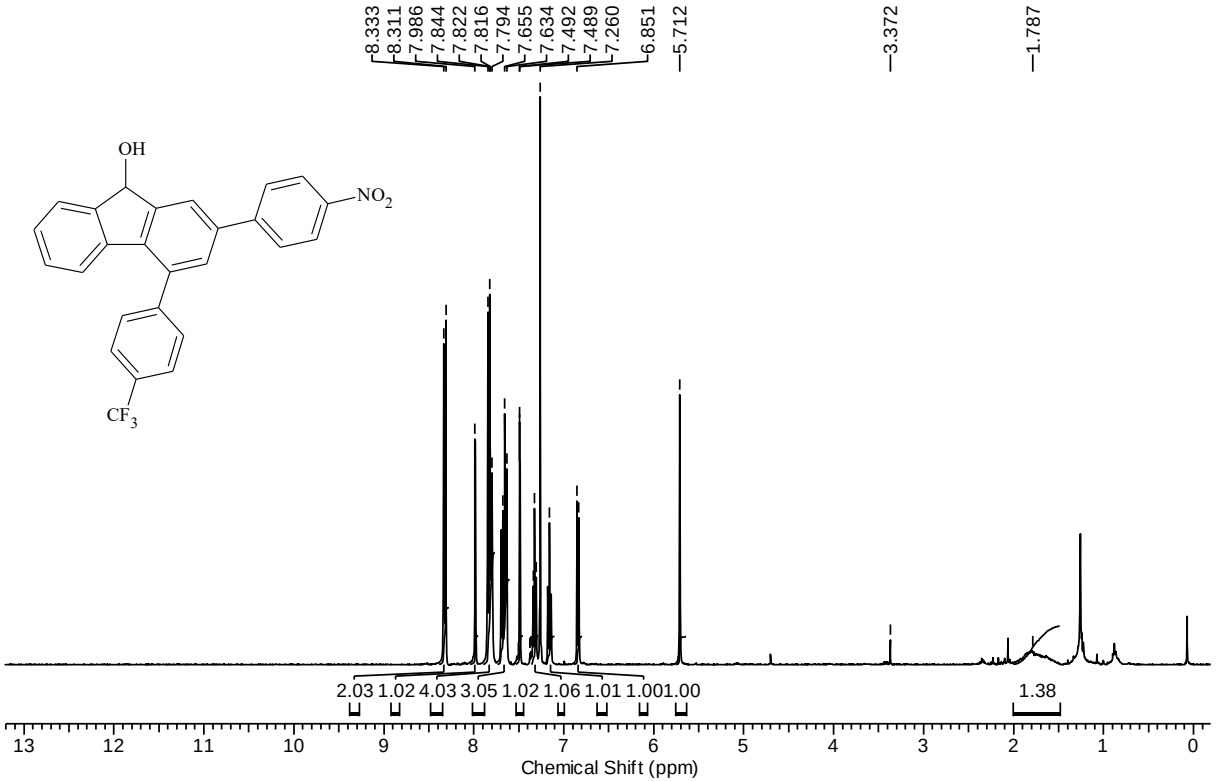


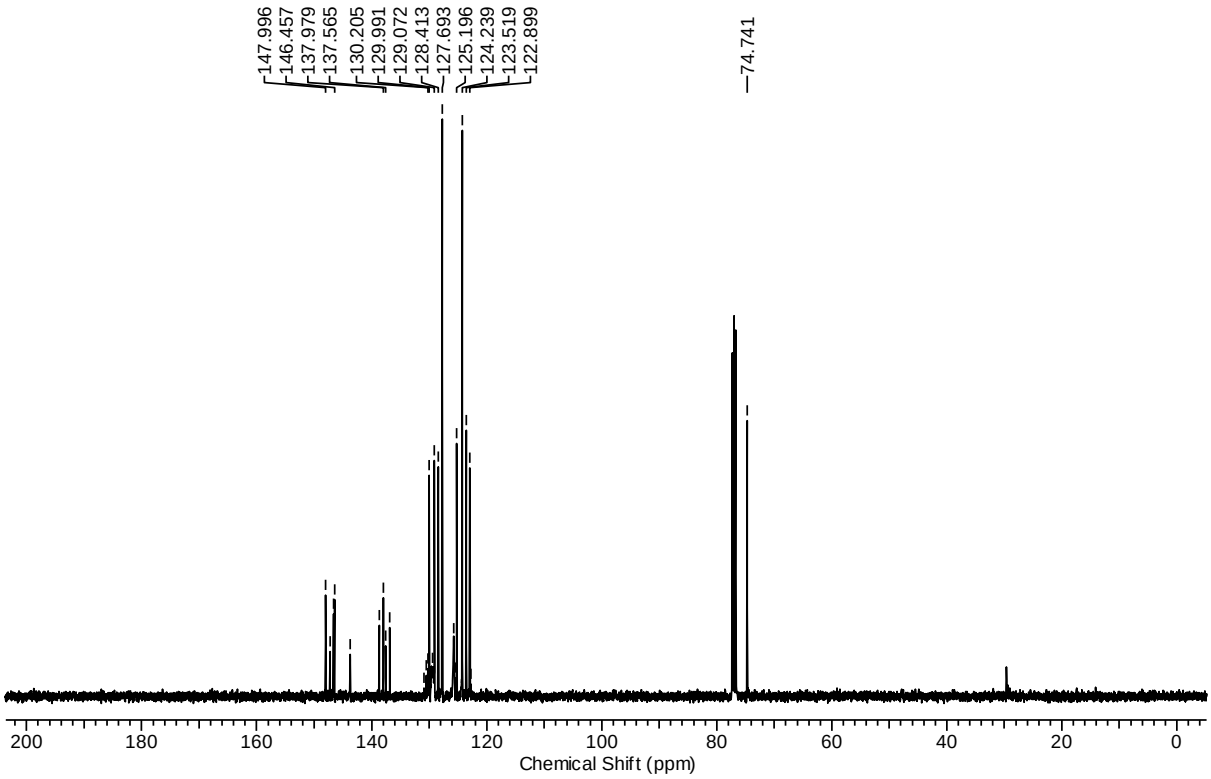
1,4-Bis(*p*-tolyl)-2-(trimethylsilyl)-9*H*-fluoren-9-one (4h) and 1,4-bis(*p*-tolyl)-3-(trimethylsilyl)-9*H*-fluoren-9-one (4'h)



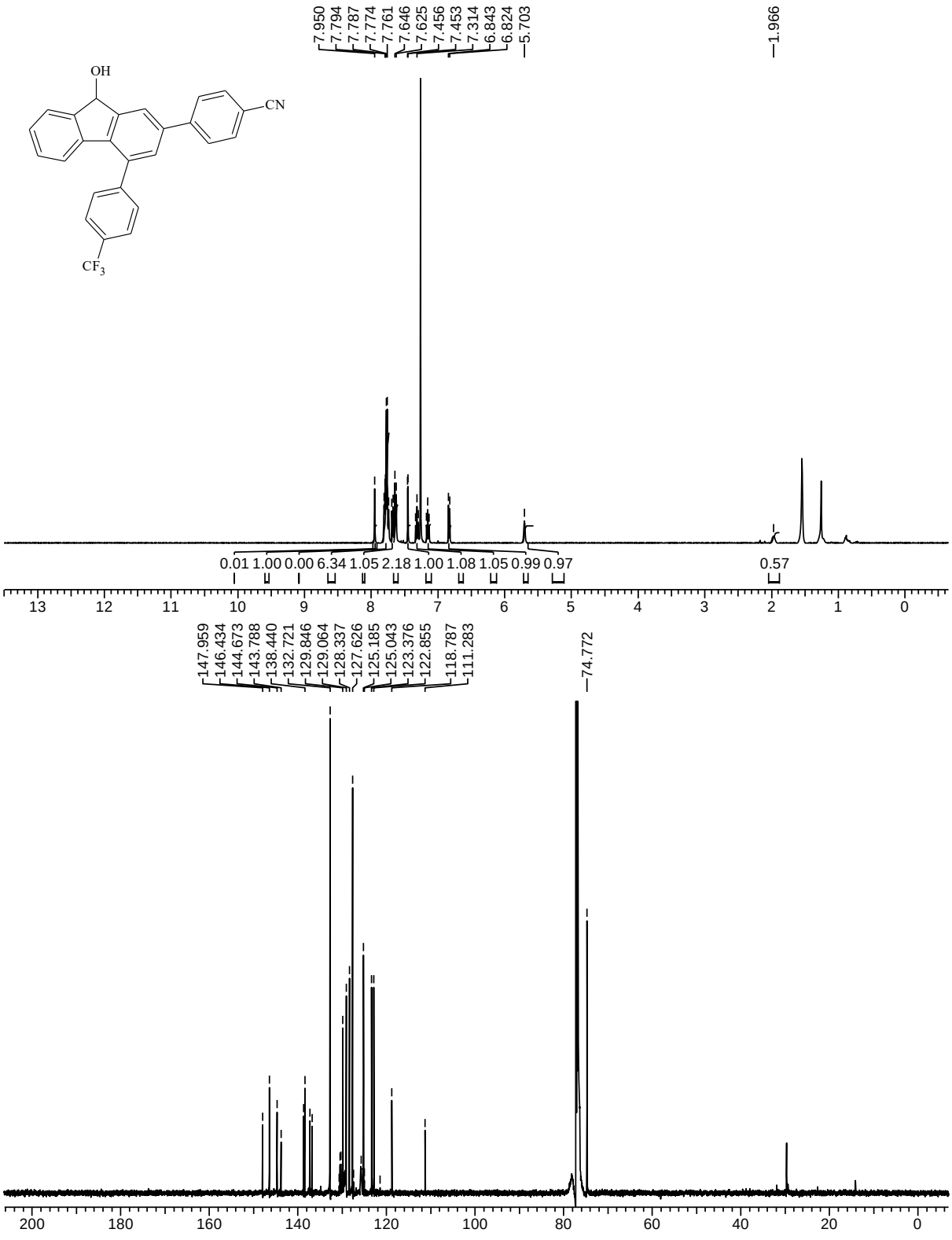


2-(4-Nitrophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6a)

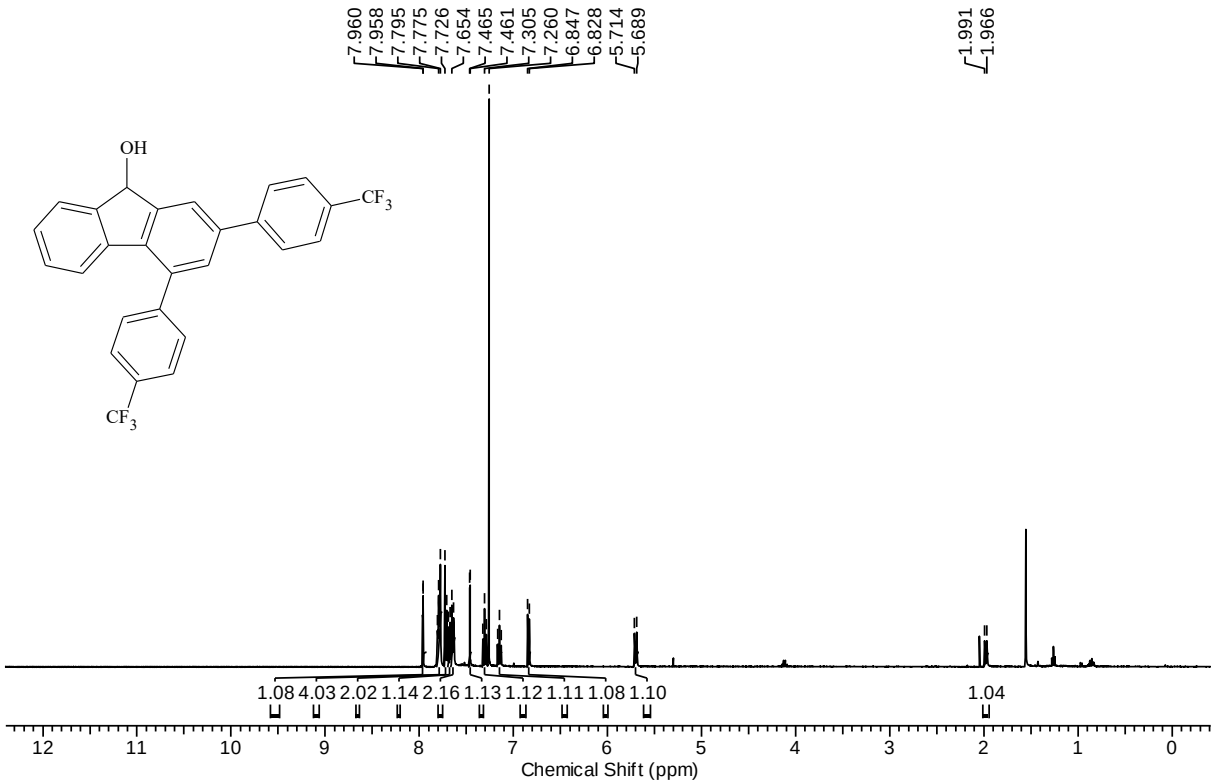


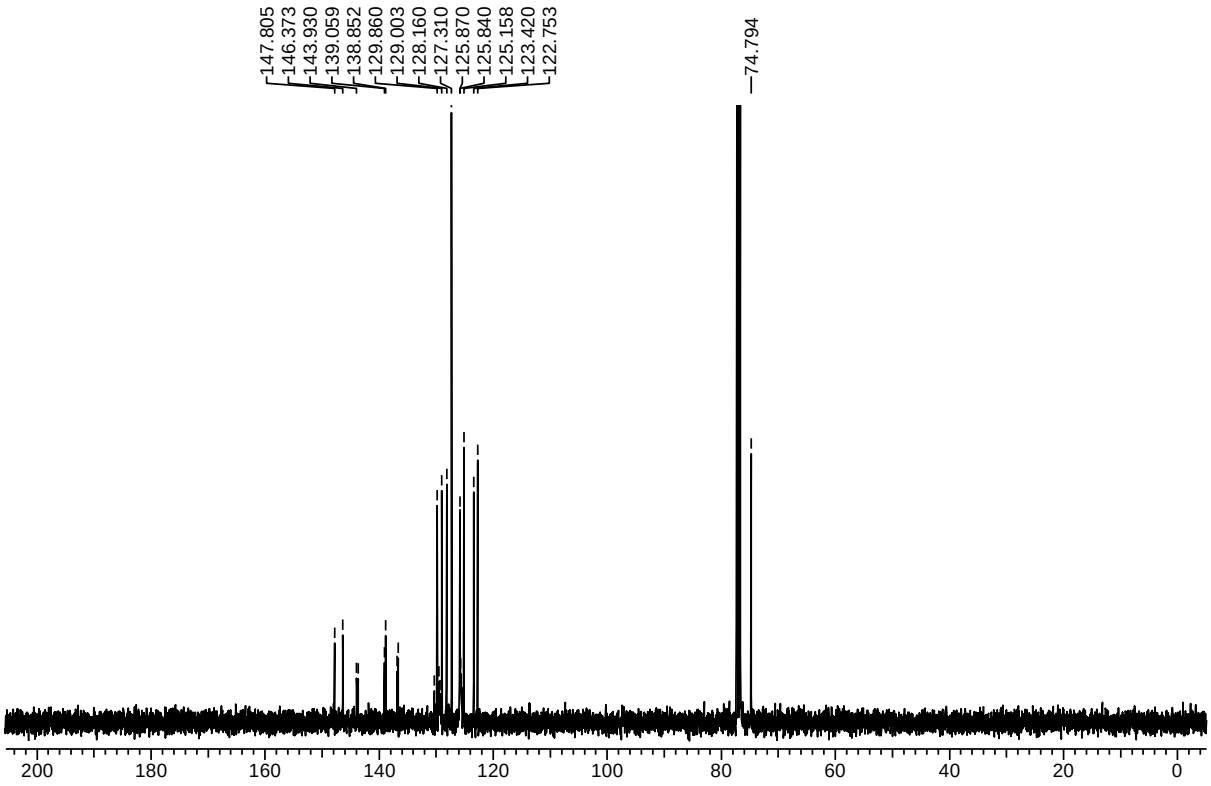


4-(9-Hydroxy-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-2-yl)benzonitrile (6b)

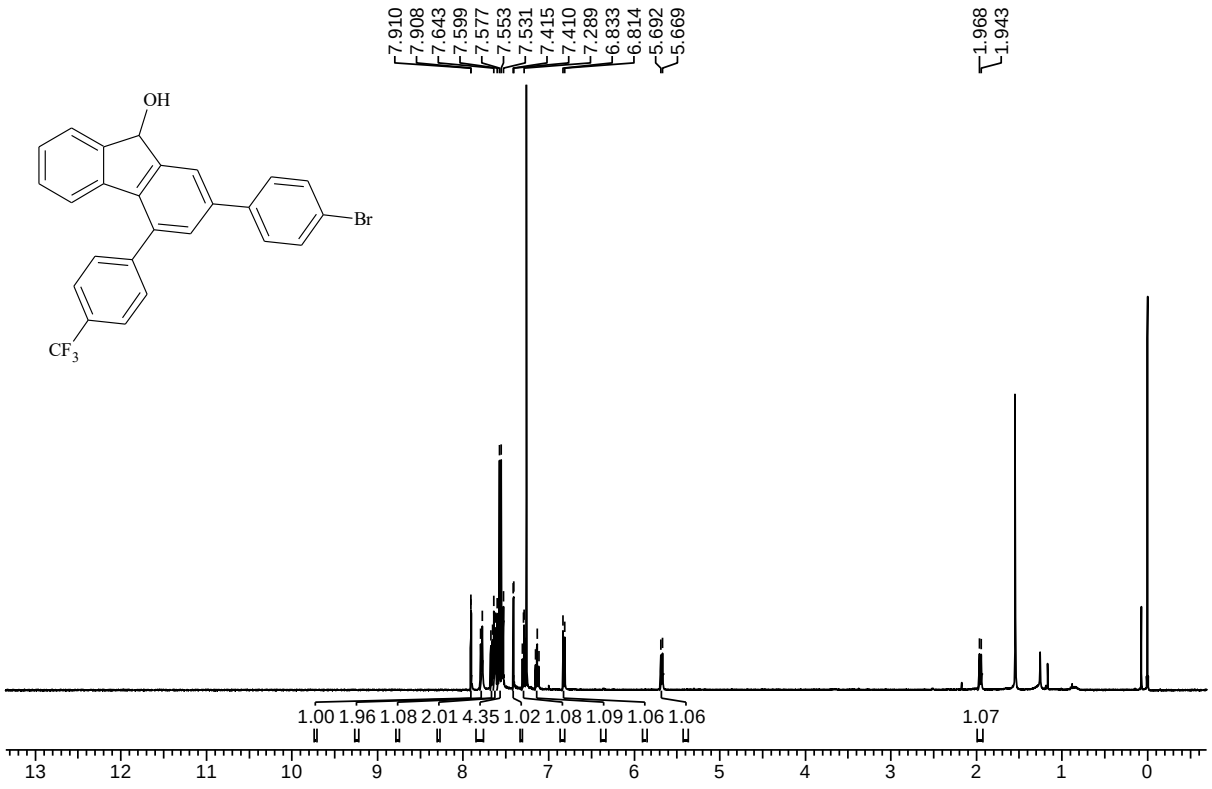


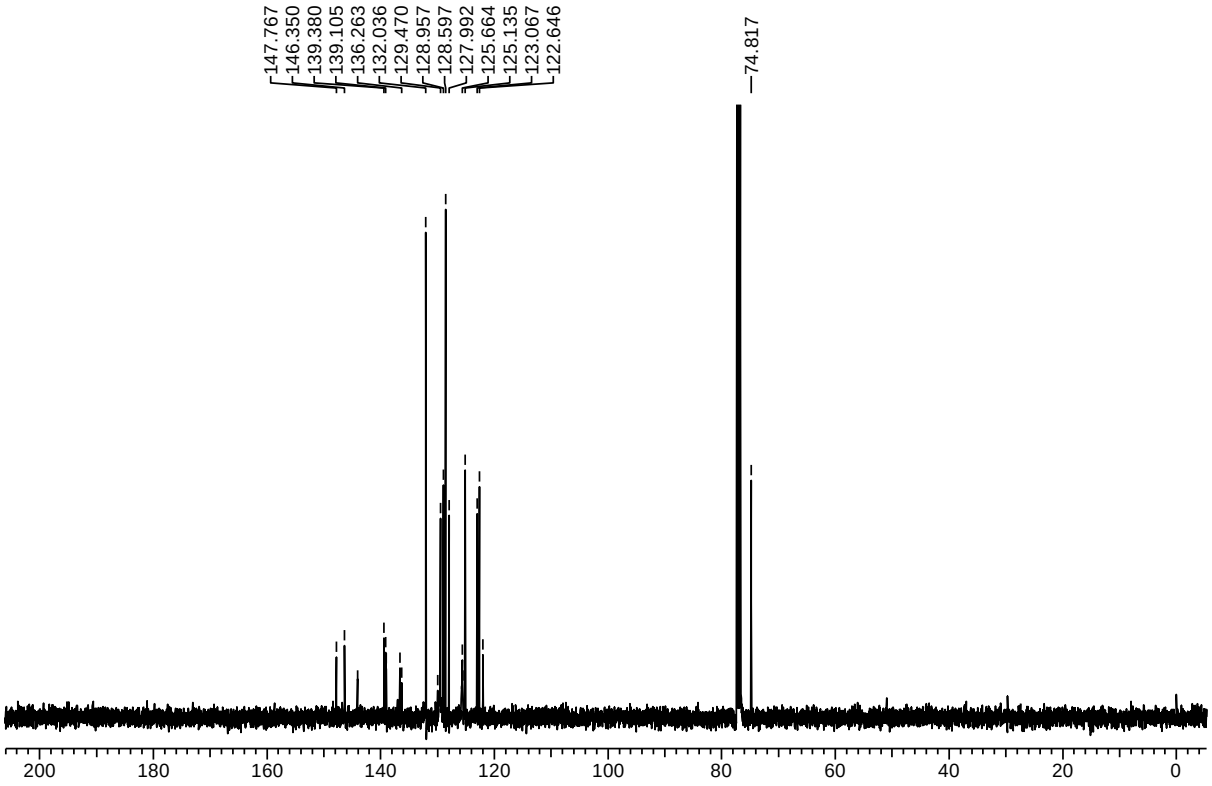
2,4-Bis(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6c)



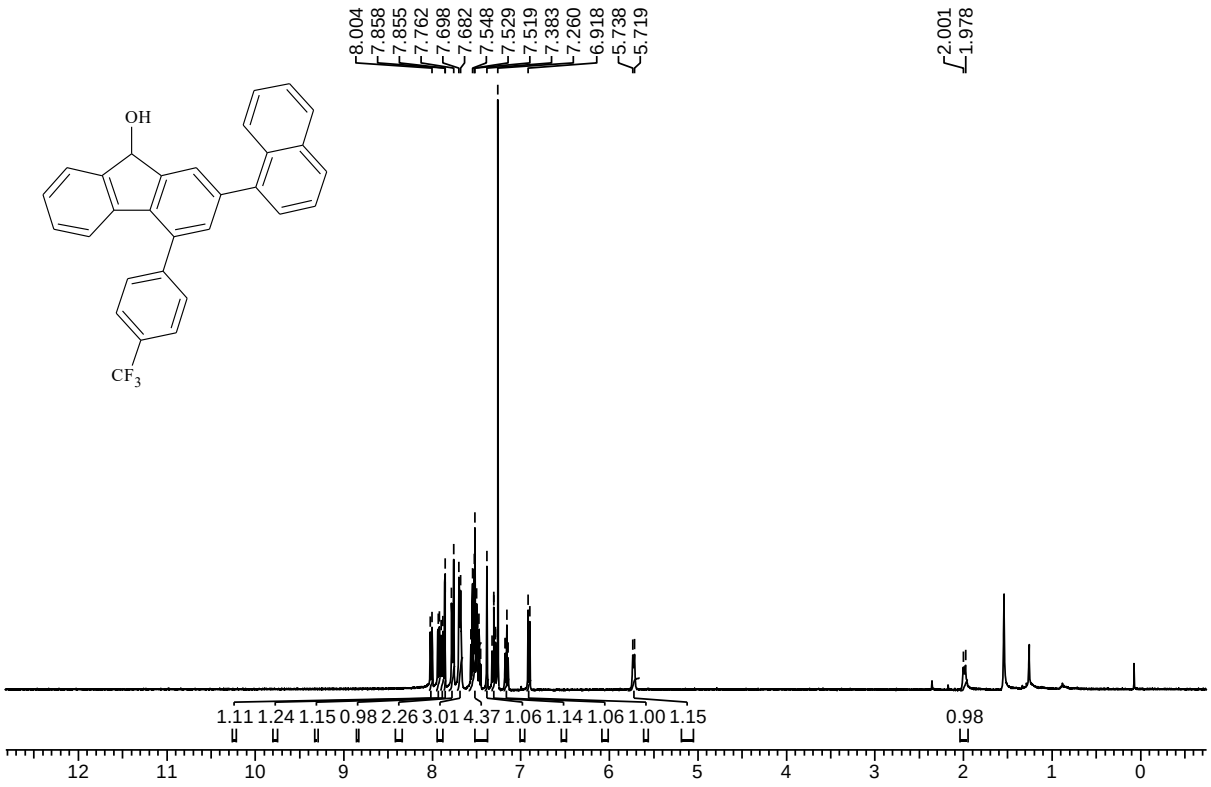


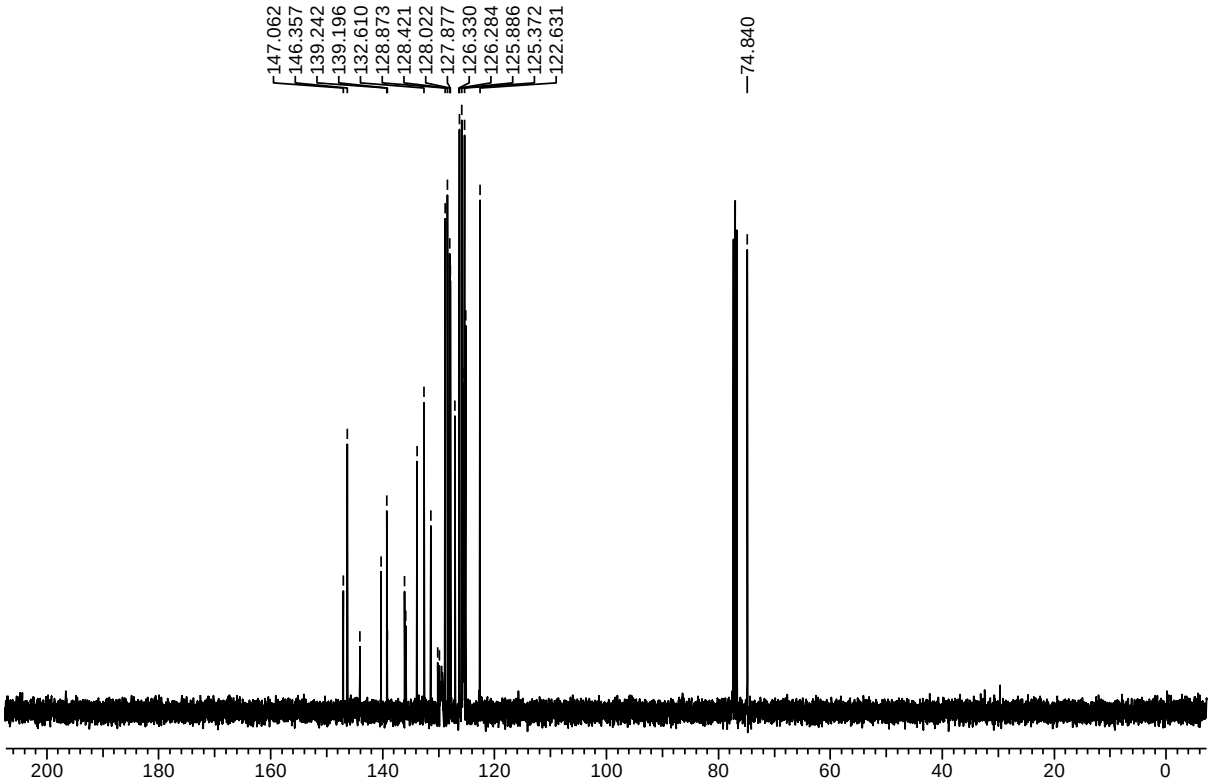
2-(4-Bromophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6d)



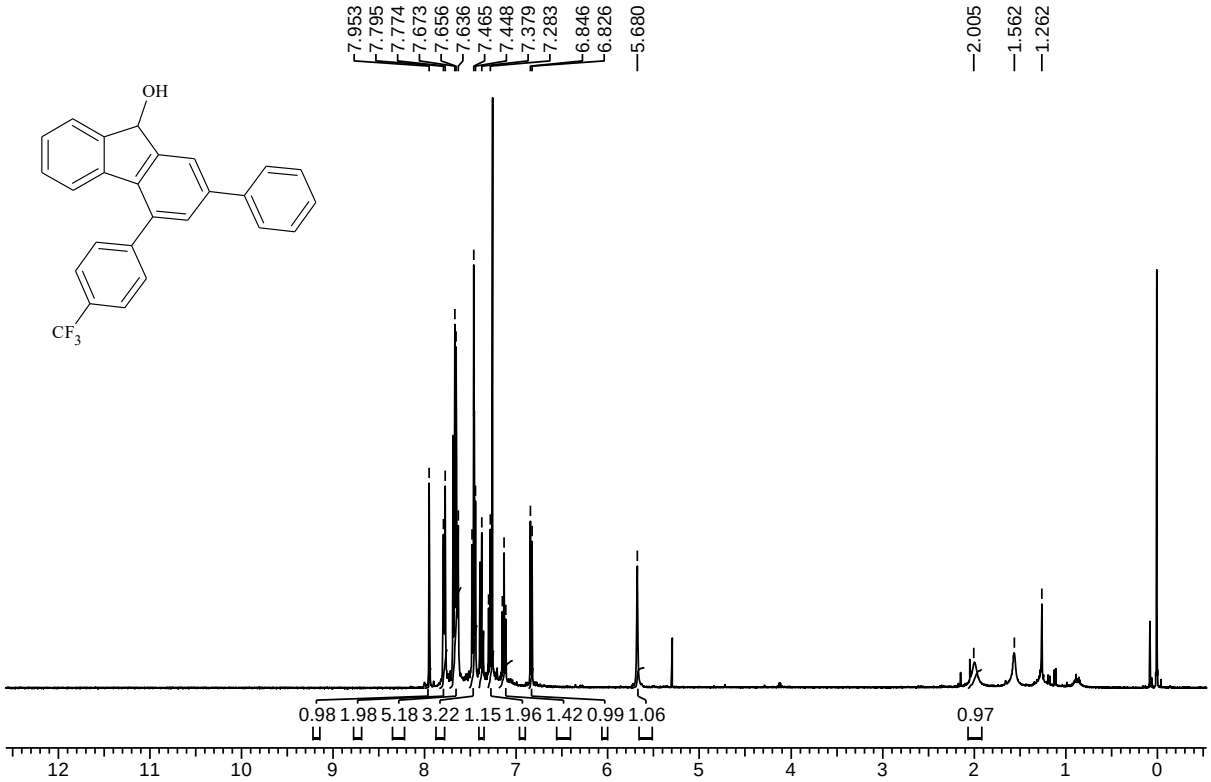


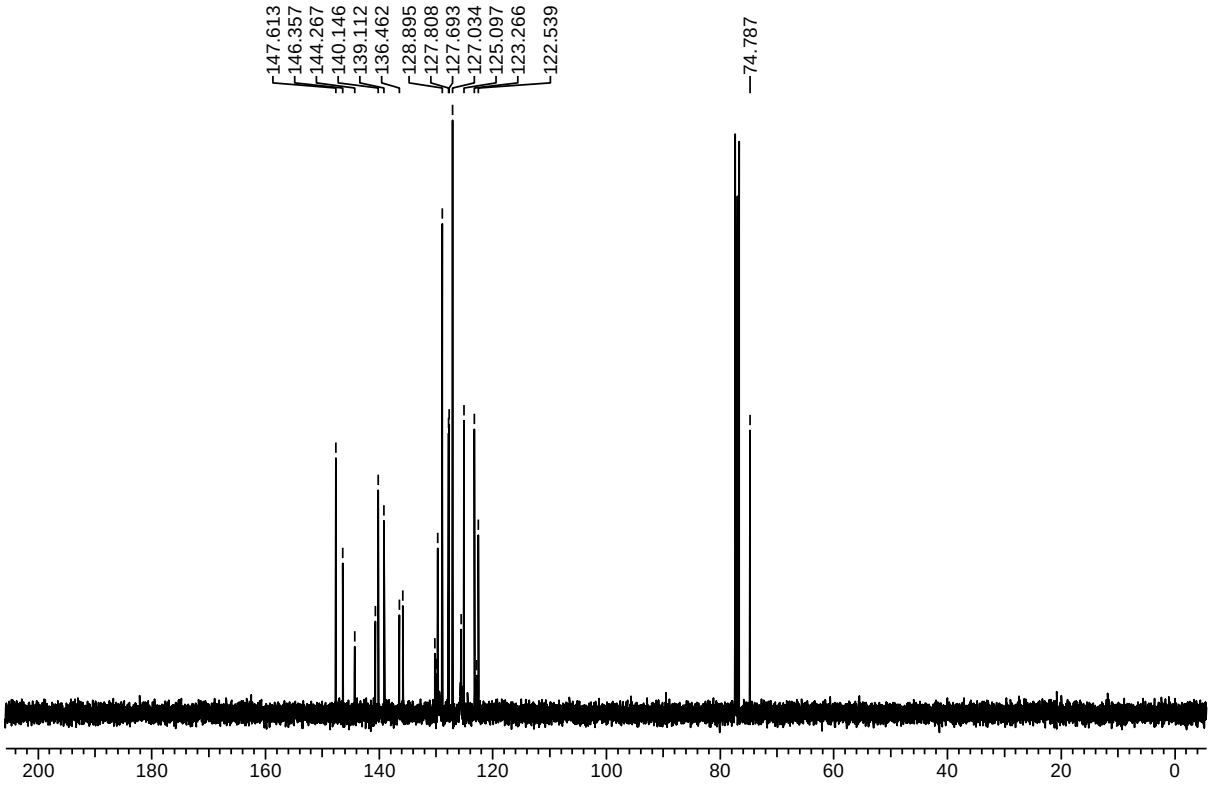
2-(Naphth-1-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6e)



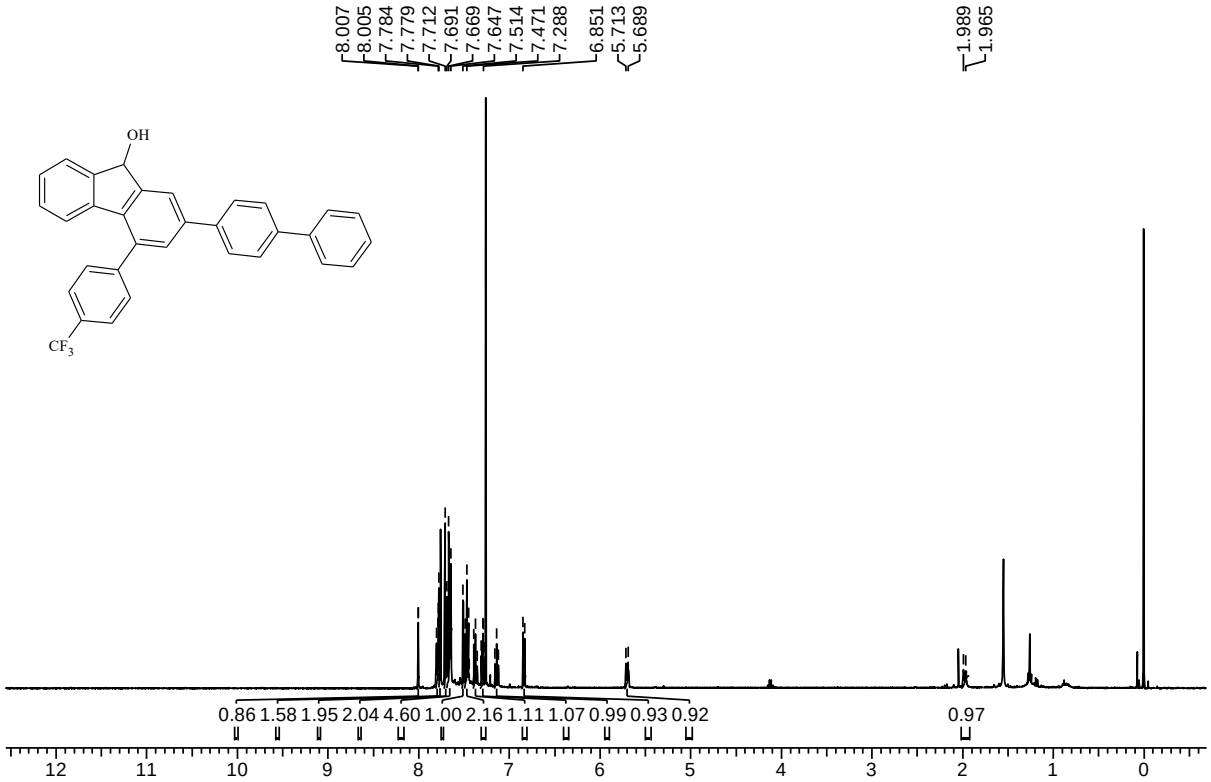


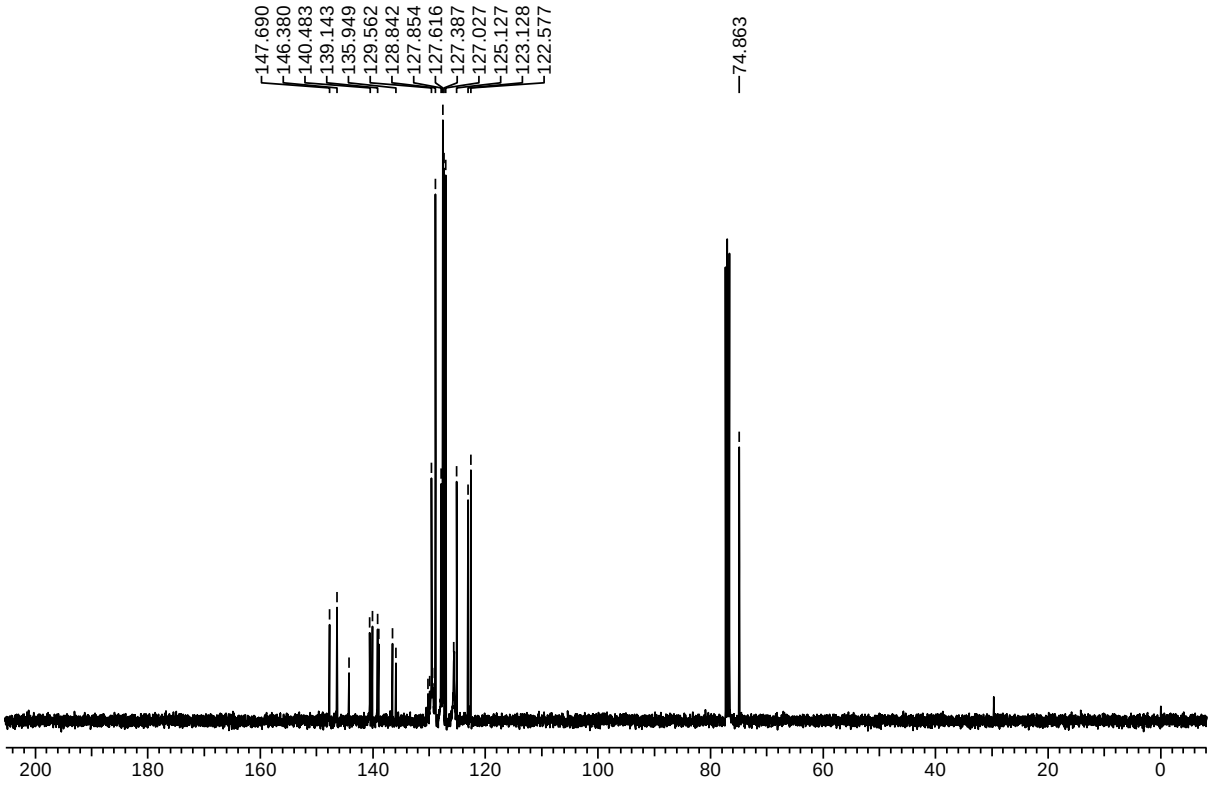
2-Phenyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6f)



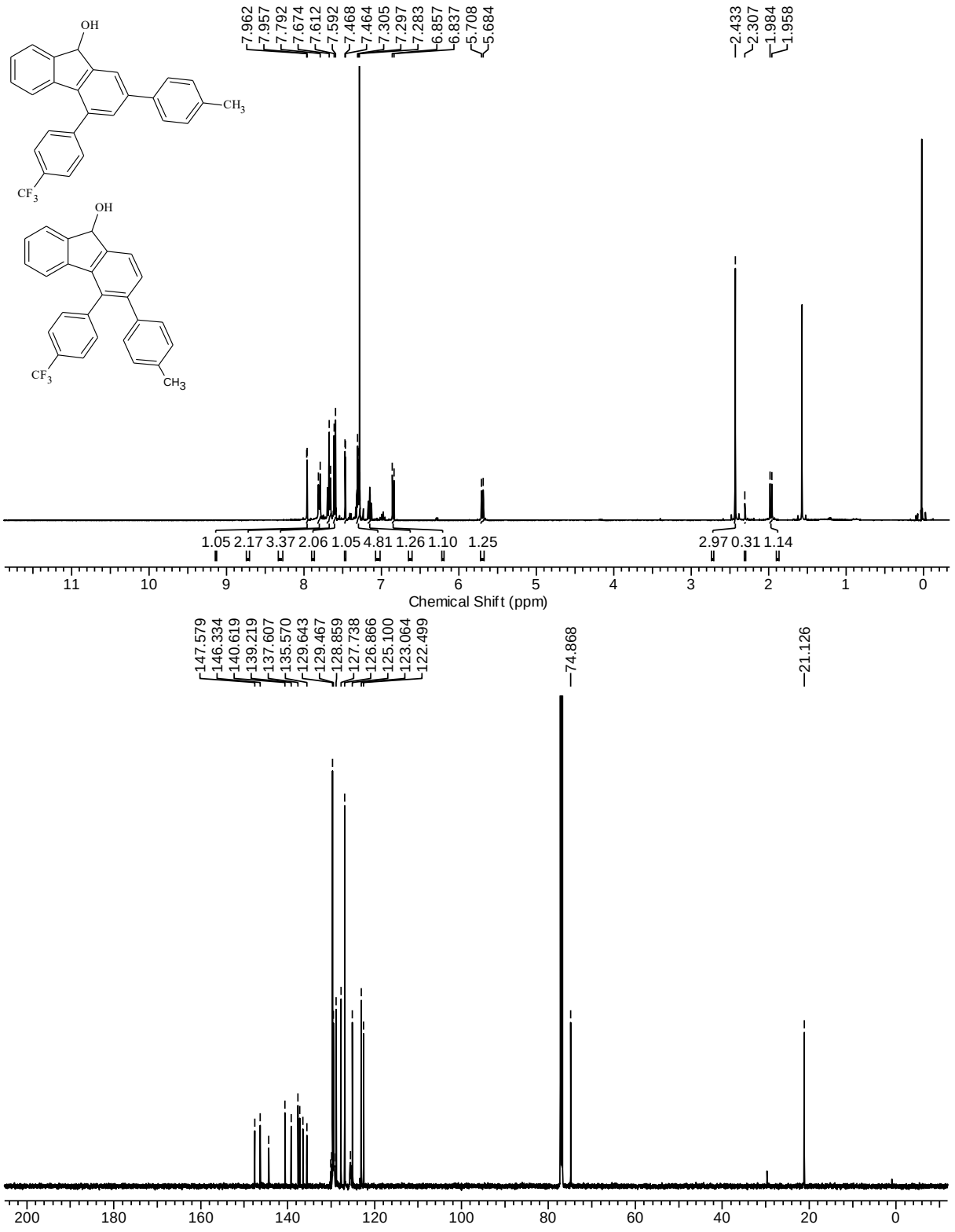


2-([1,1'-Biphenyl]-4-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6g)

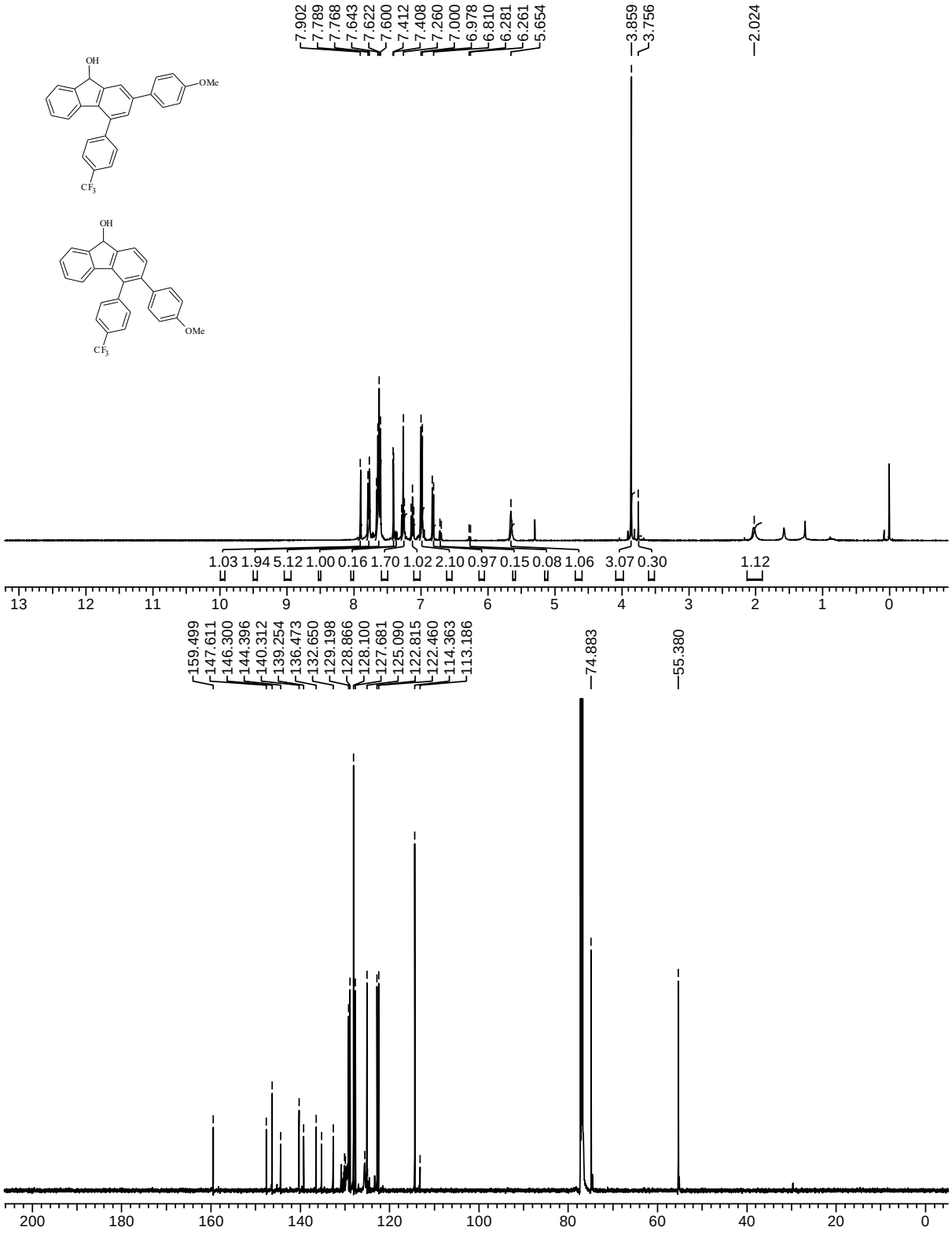




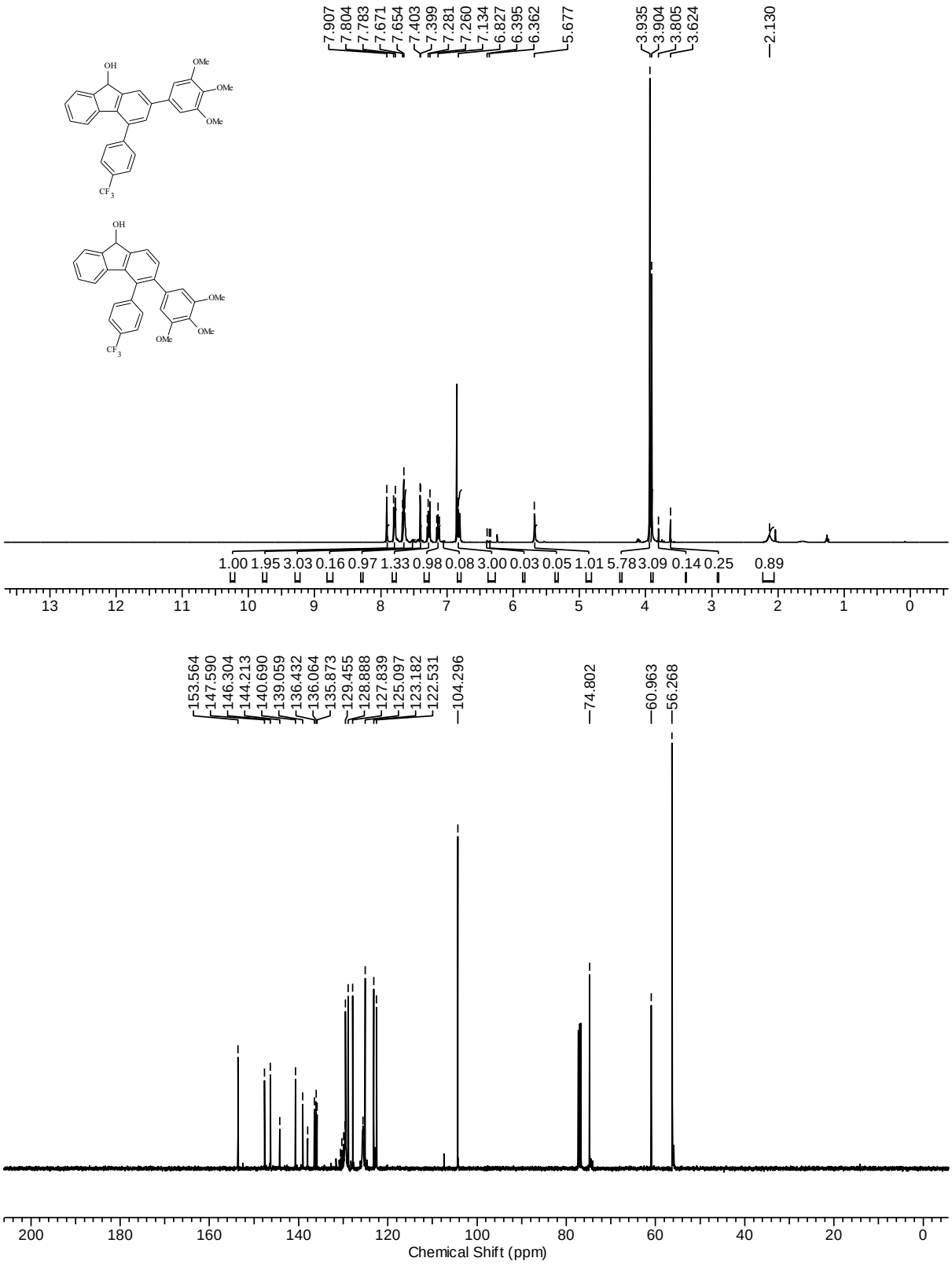
2-(*p*-Tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6h)



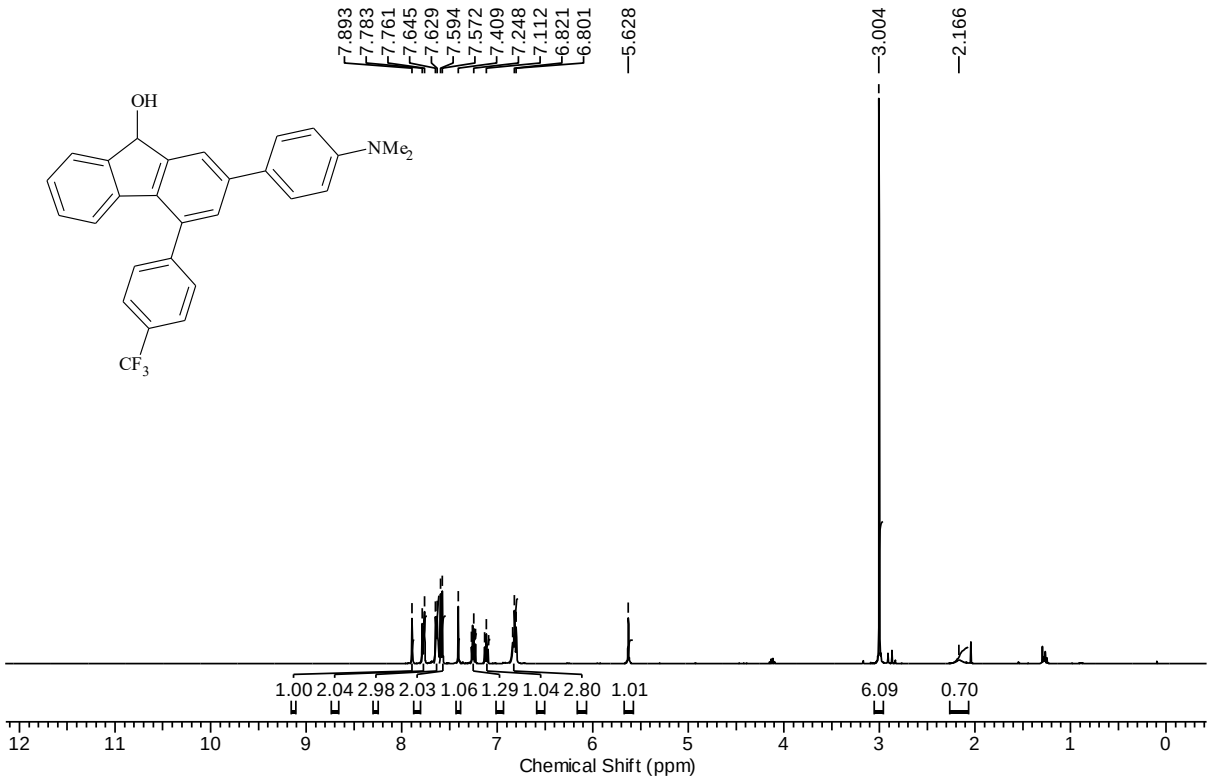
2-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-9H-fluoren-9-ol (6i)

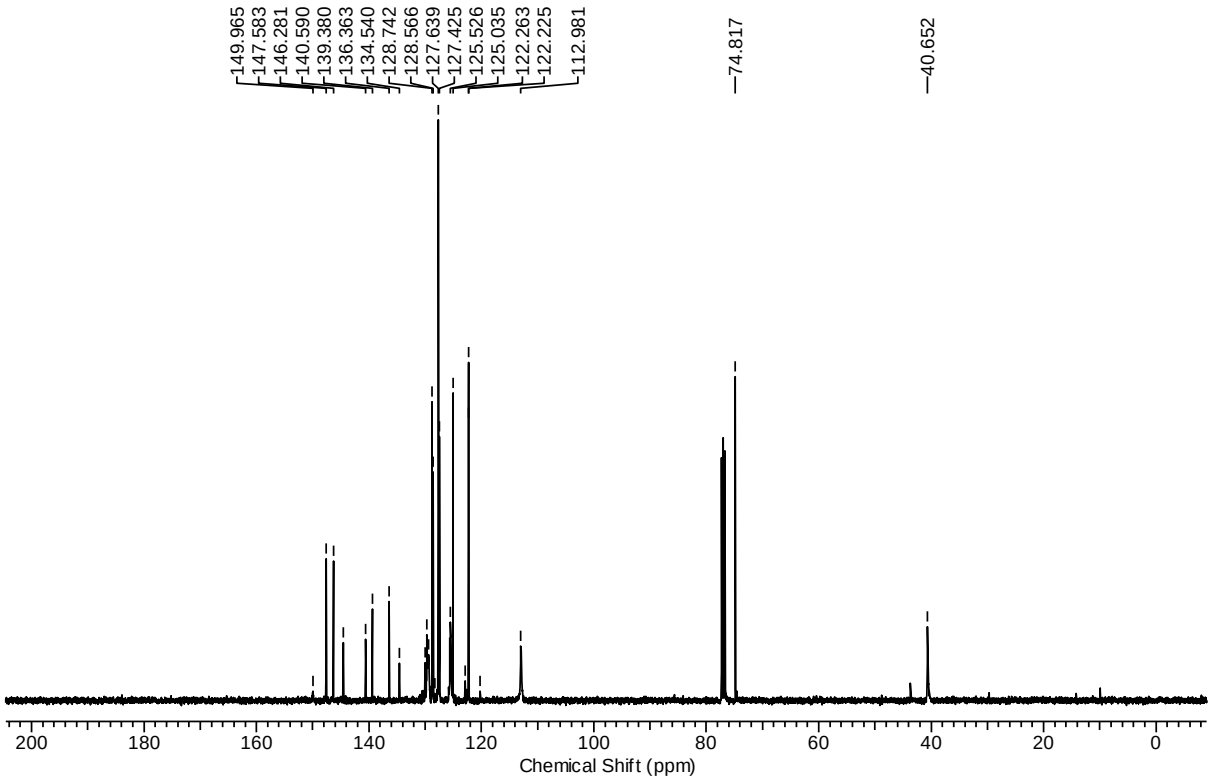


4-(4-(Trifluoromethyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-9*H*-fluoren-9-ol (6j)

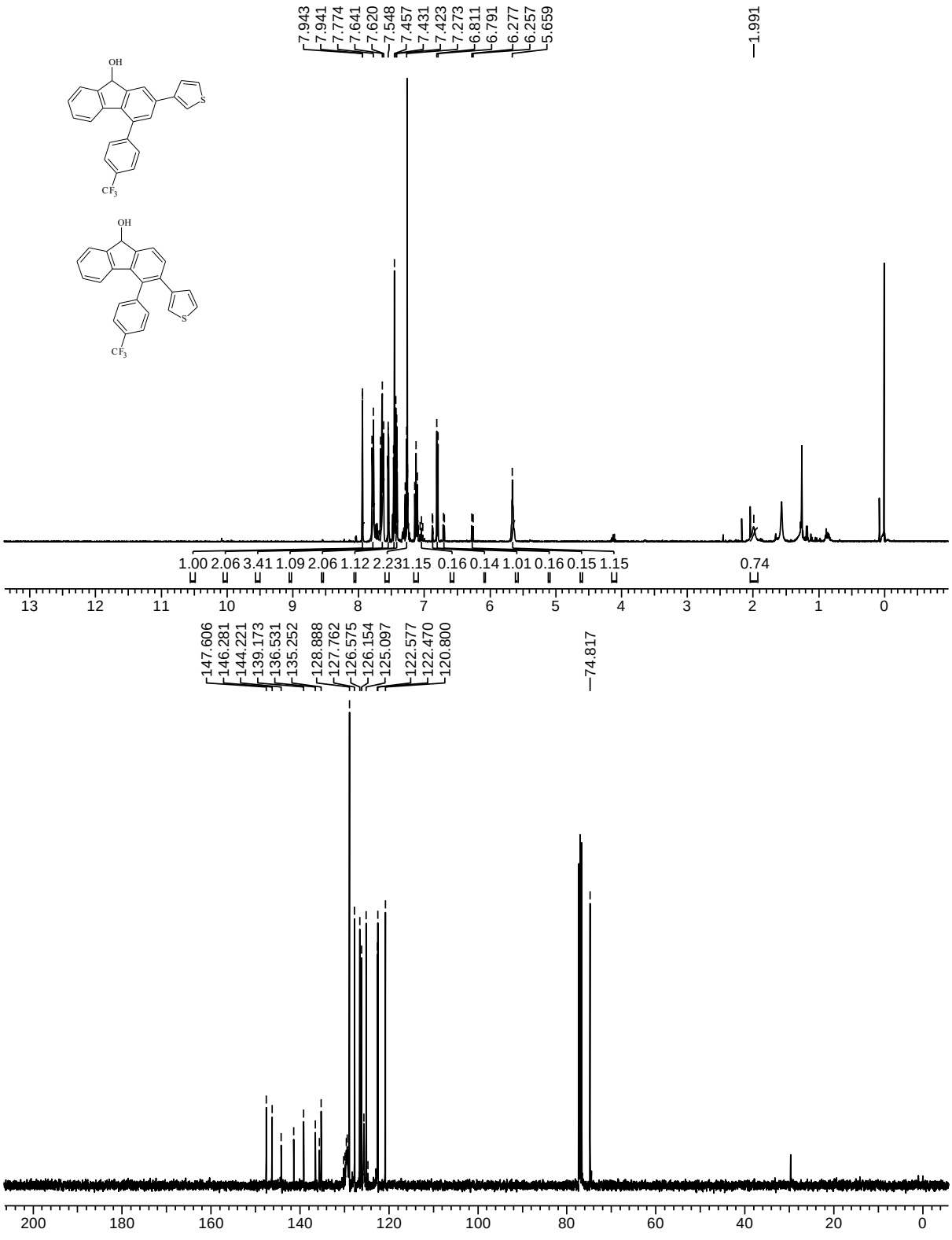


2-(4-(*N*,*N*-dimethylamino)phenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6k)

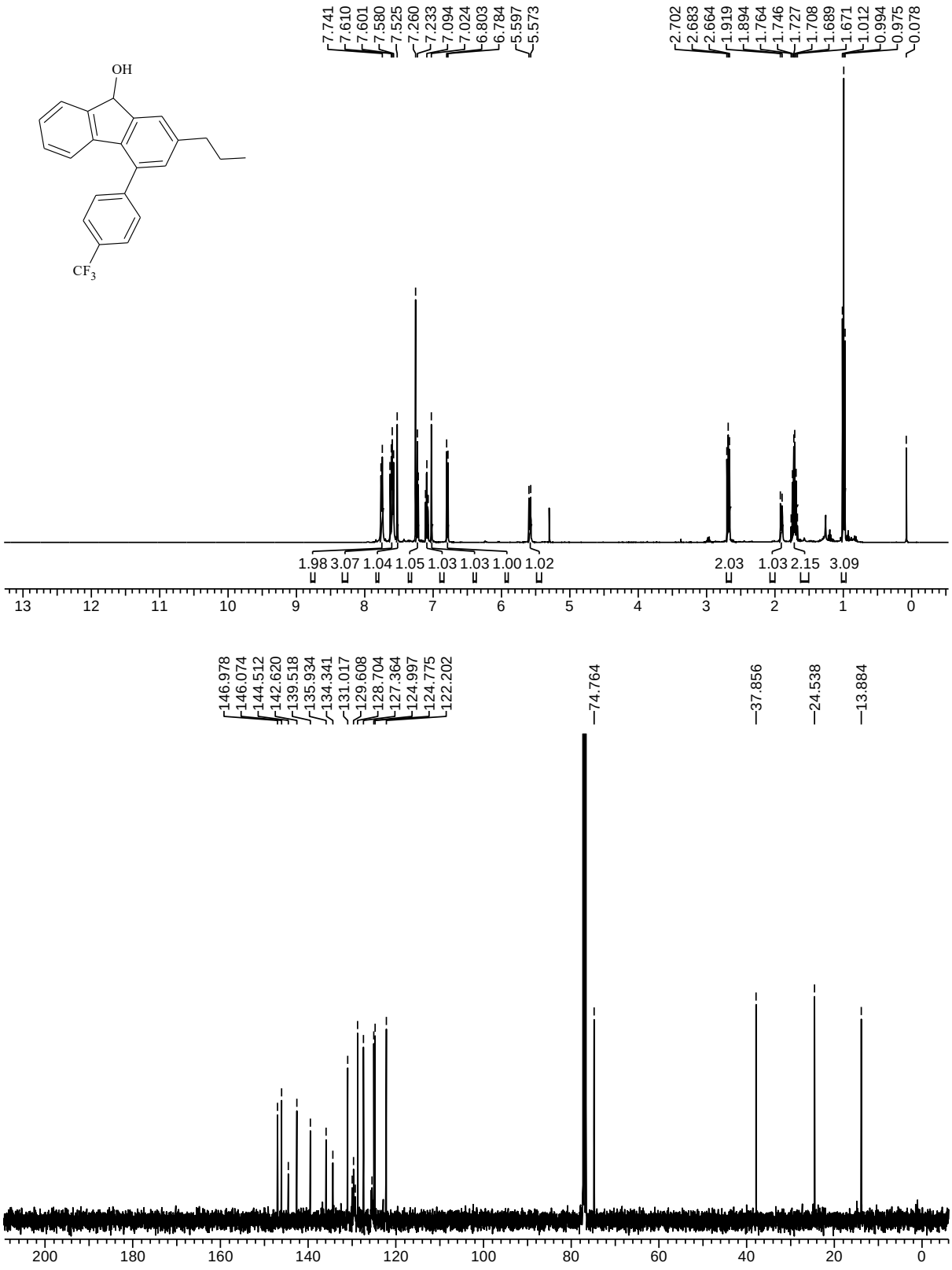




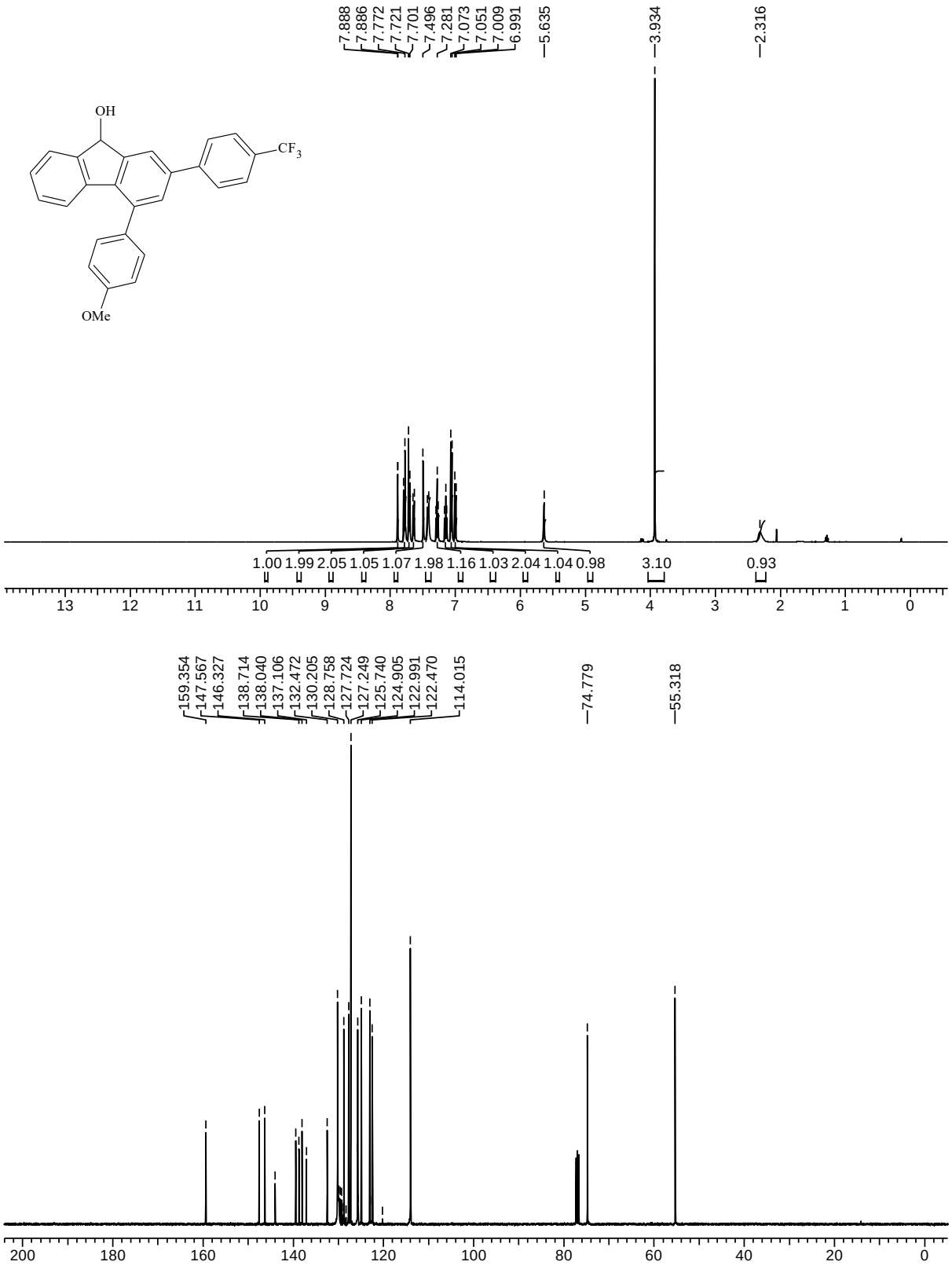
2-(Ihien-3-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6l)



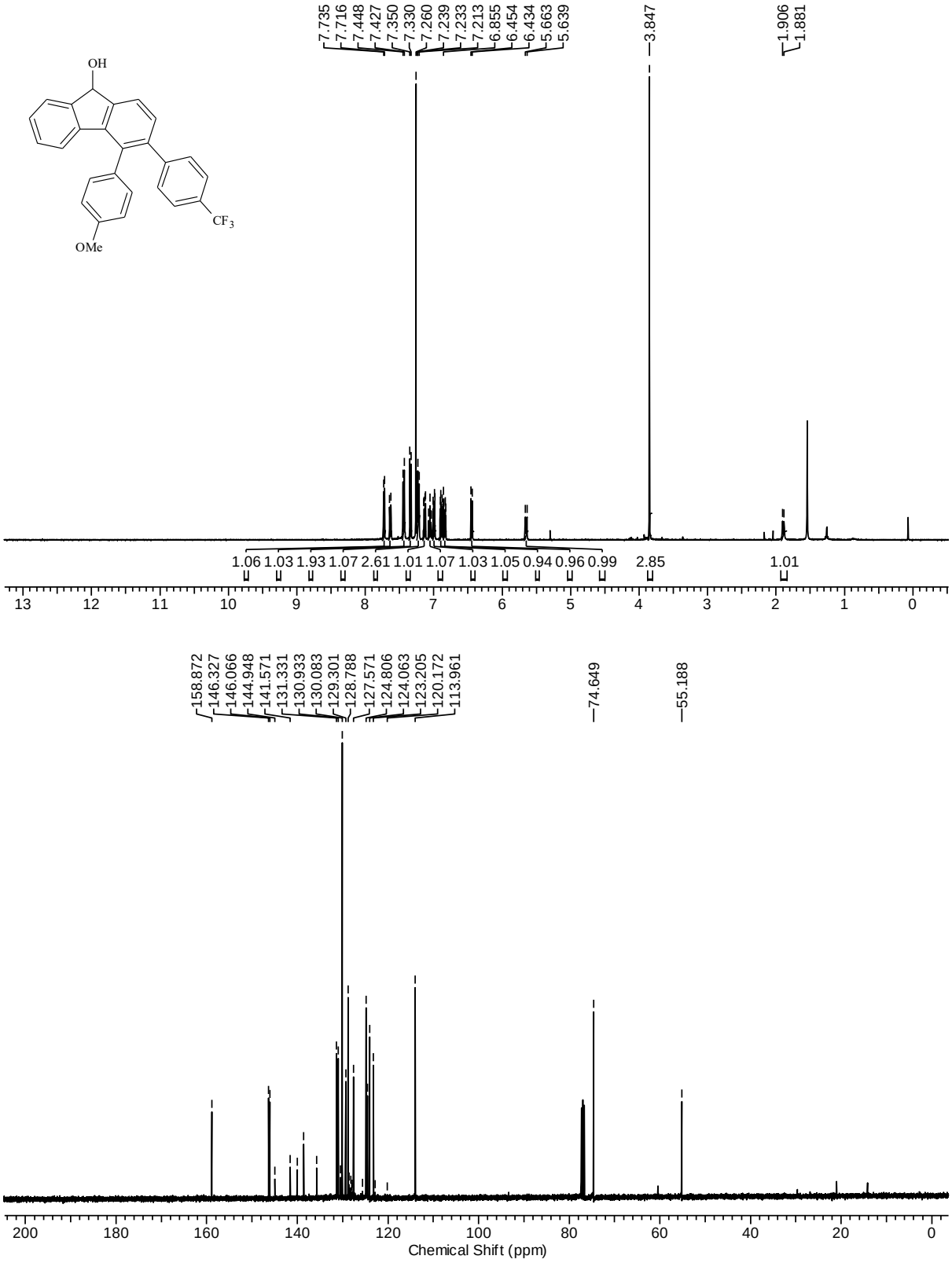
2-Propyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6m)



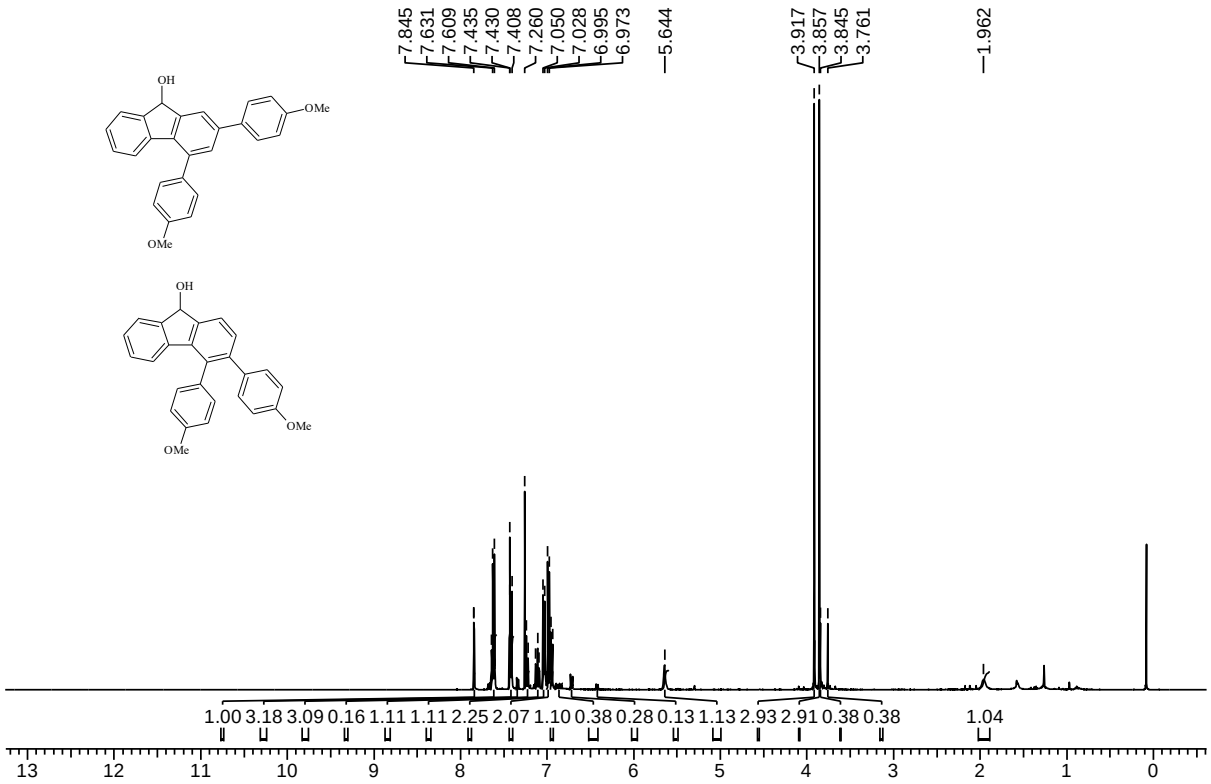
4-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-*9H*-fluoren-9-ol (6n)

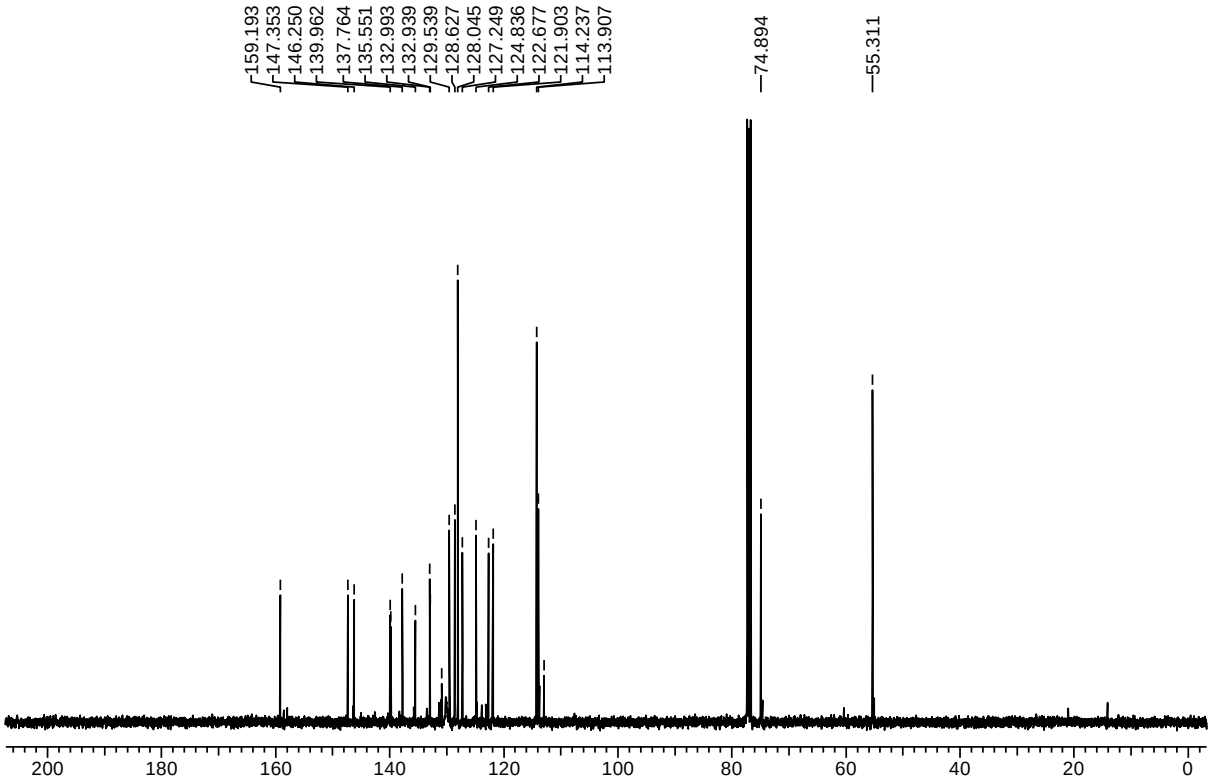


4-(4-Methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (6n')

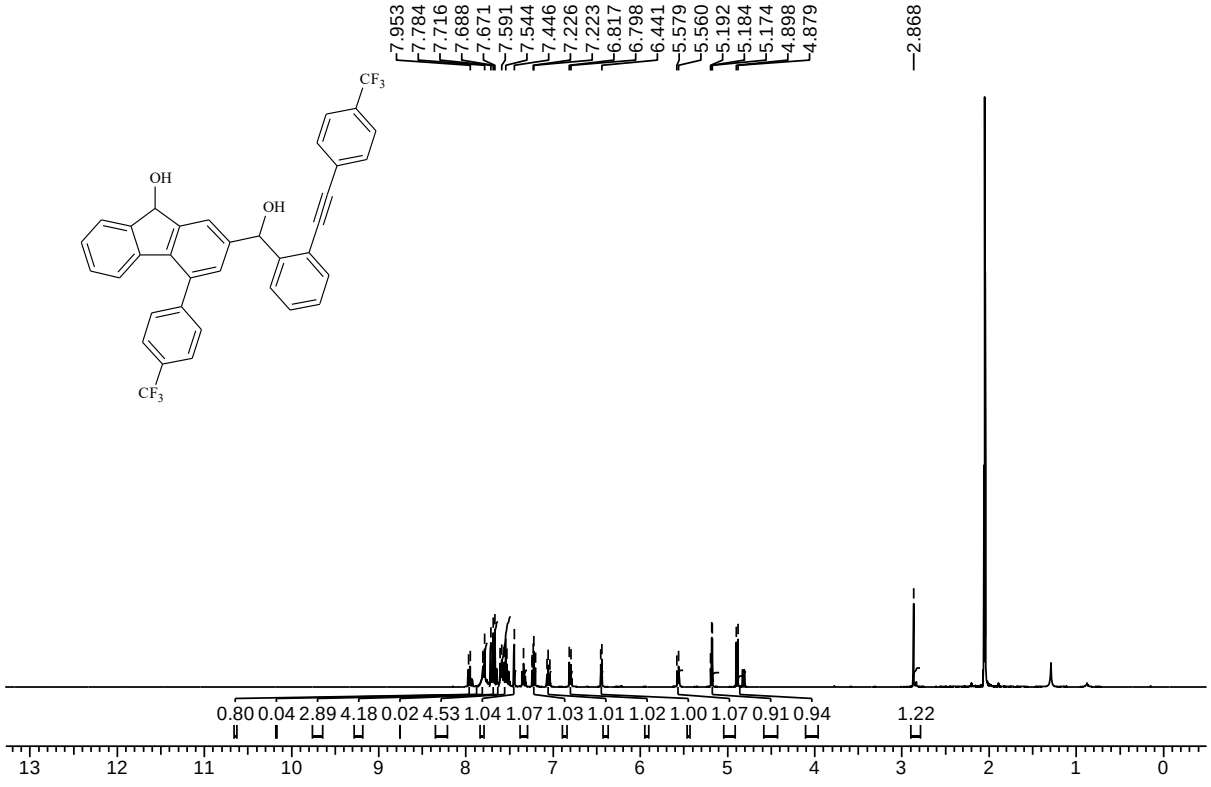


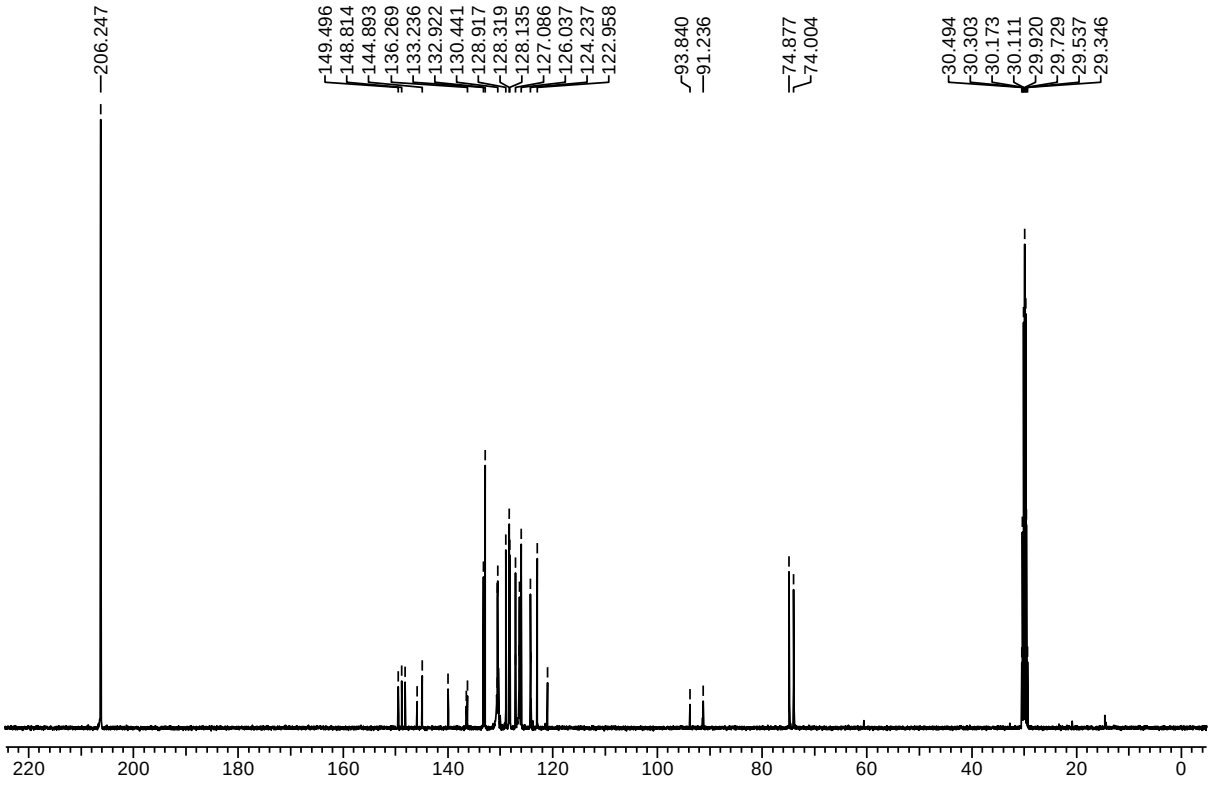
2,4-Bis(4-methoxyphenyl)-9*H*-fluoren-9-ol (6o)



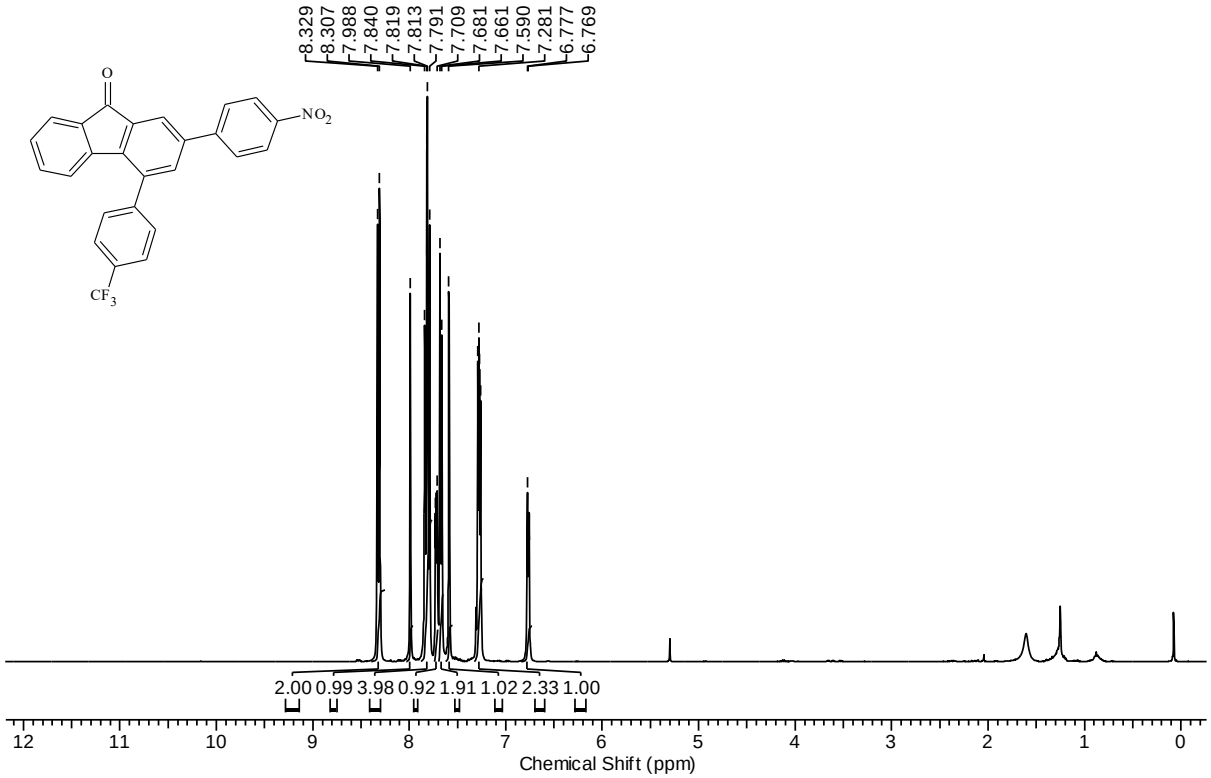


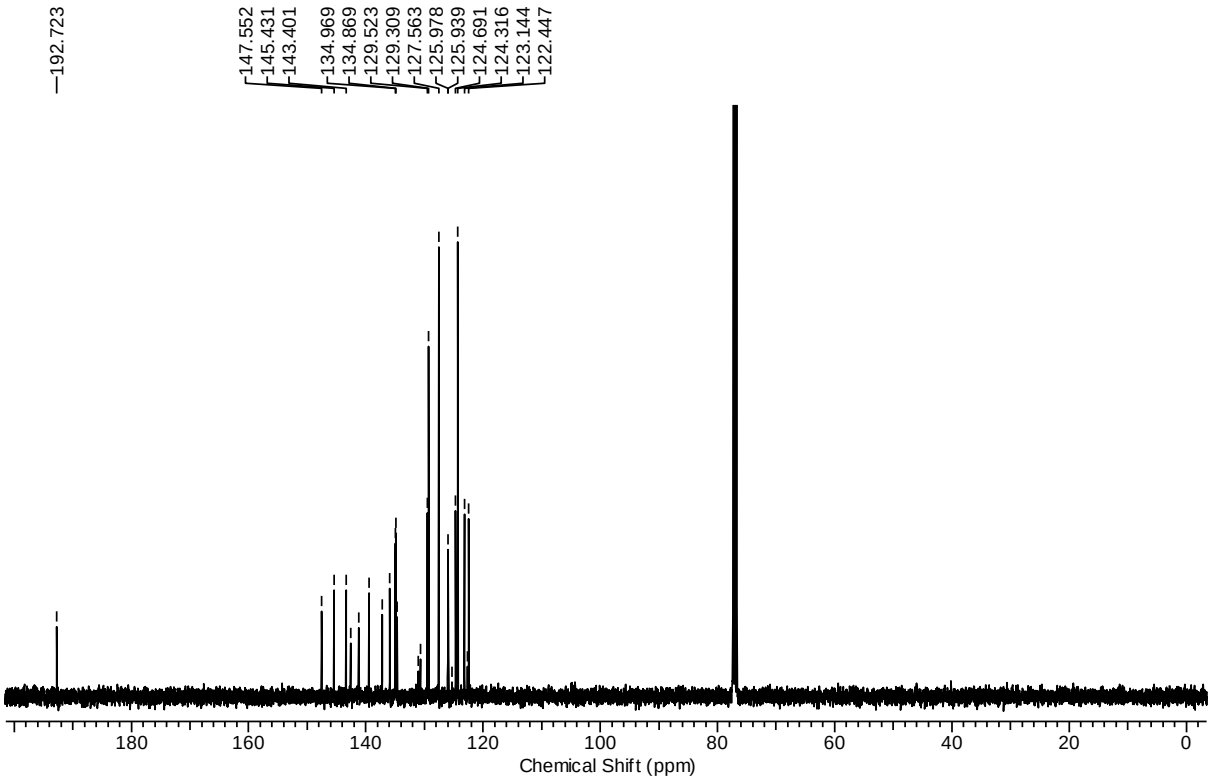
2-(Hydroxy(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)methyl)-4-(4-(trifluoromethyl) phenyl)-9*H*-fluoren-9-ol (7)



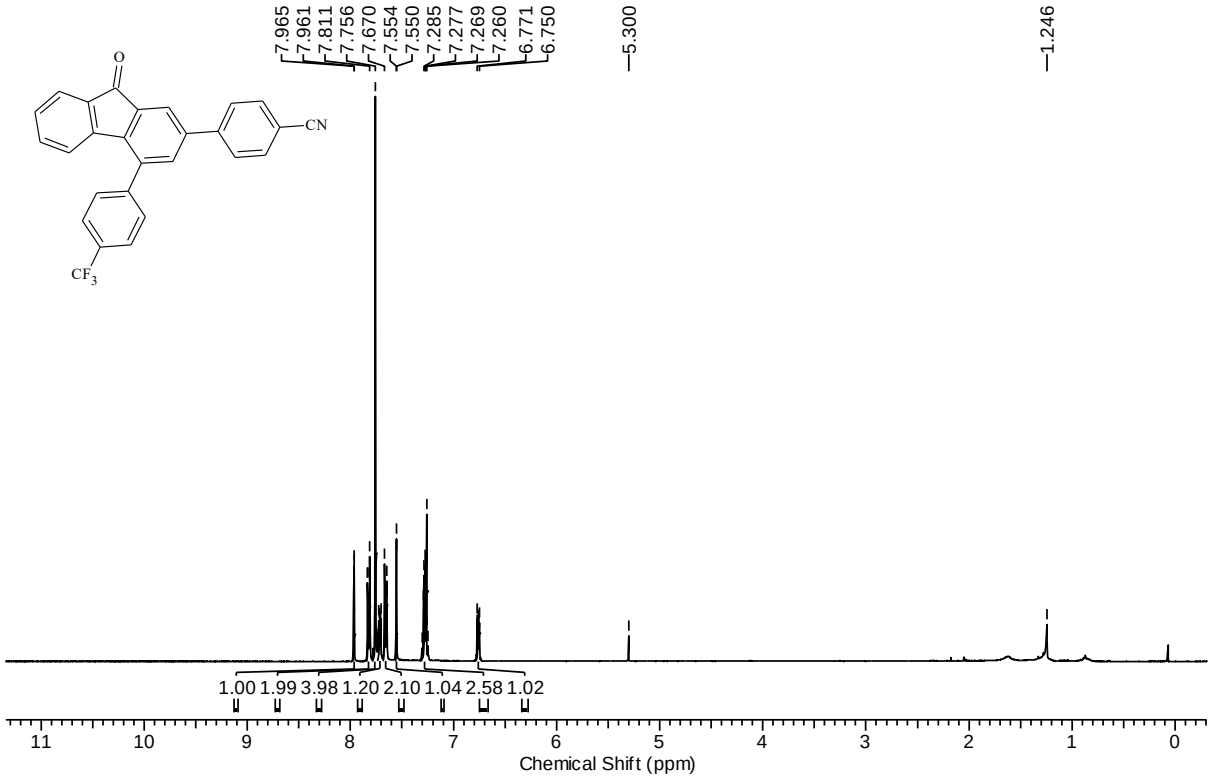


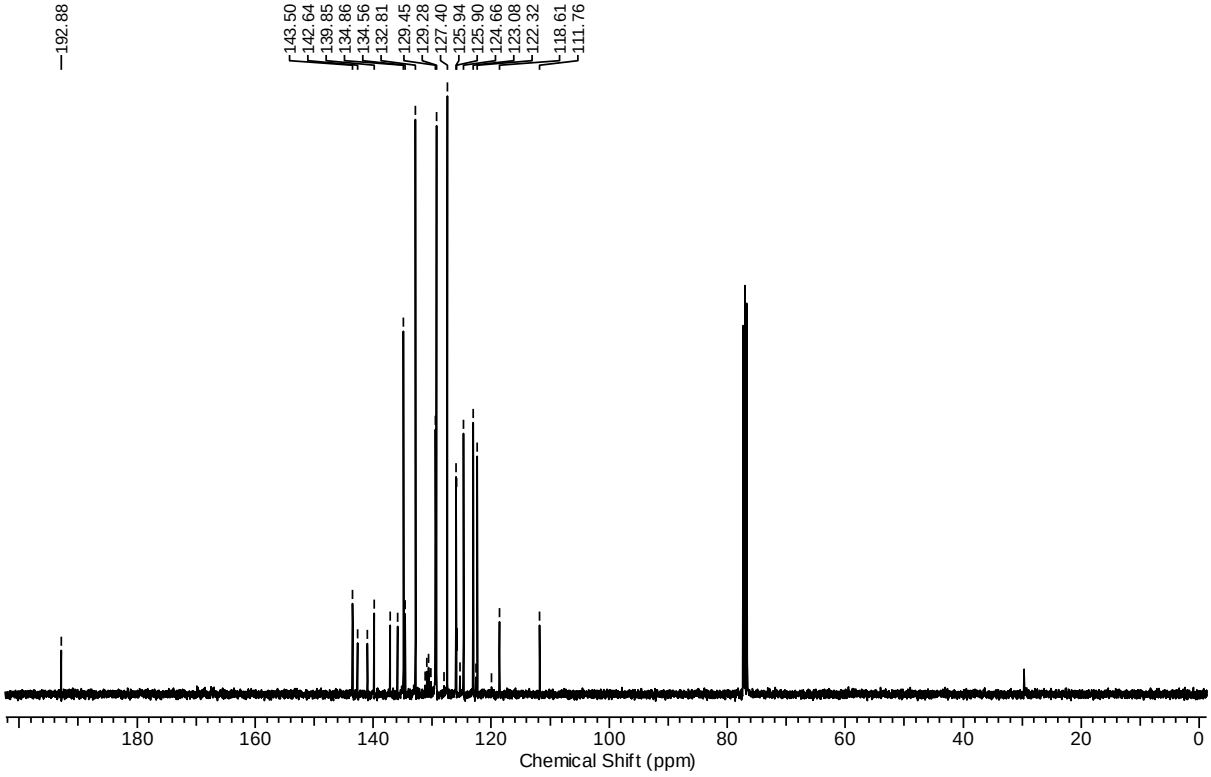
2-(4-Nitrophenyl)-4-(4-(trifluoromethyl)phenyl)-*9H*-fluoren-9-one (8a)



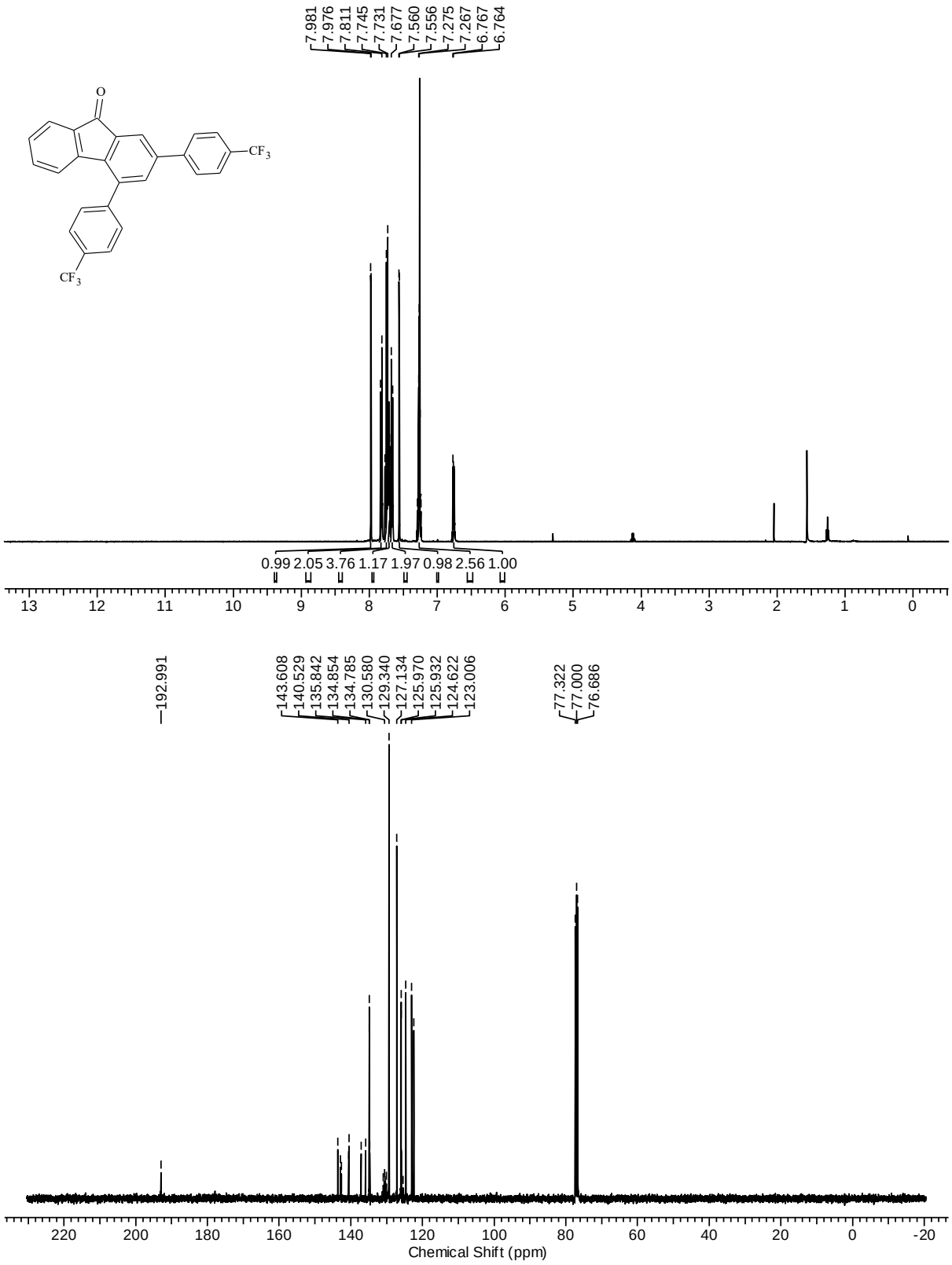


4-(9-Oxo-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-2-yl)benzonitrile (8b)

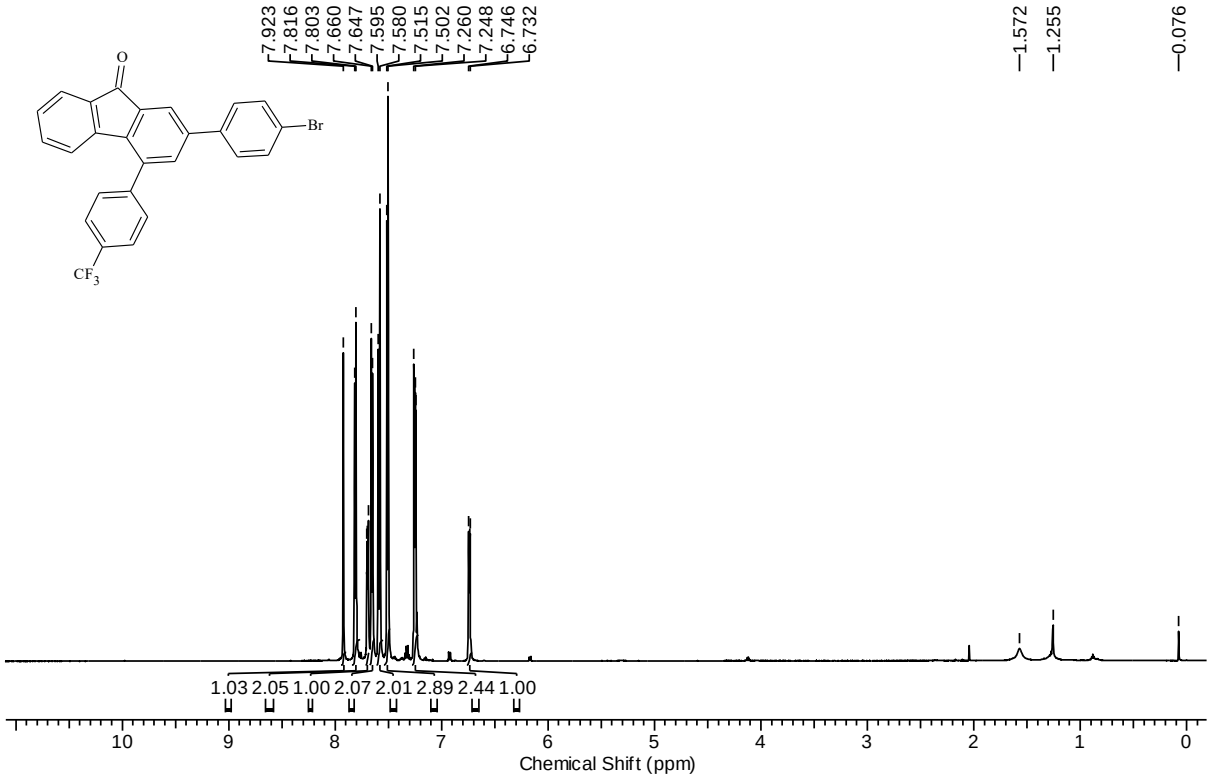


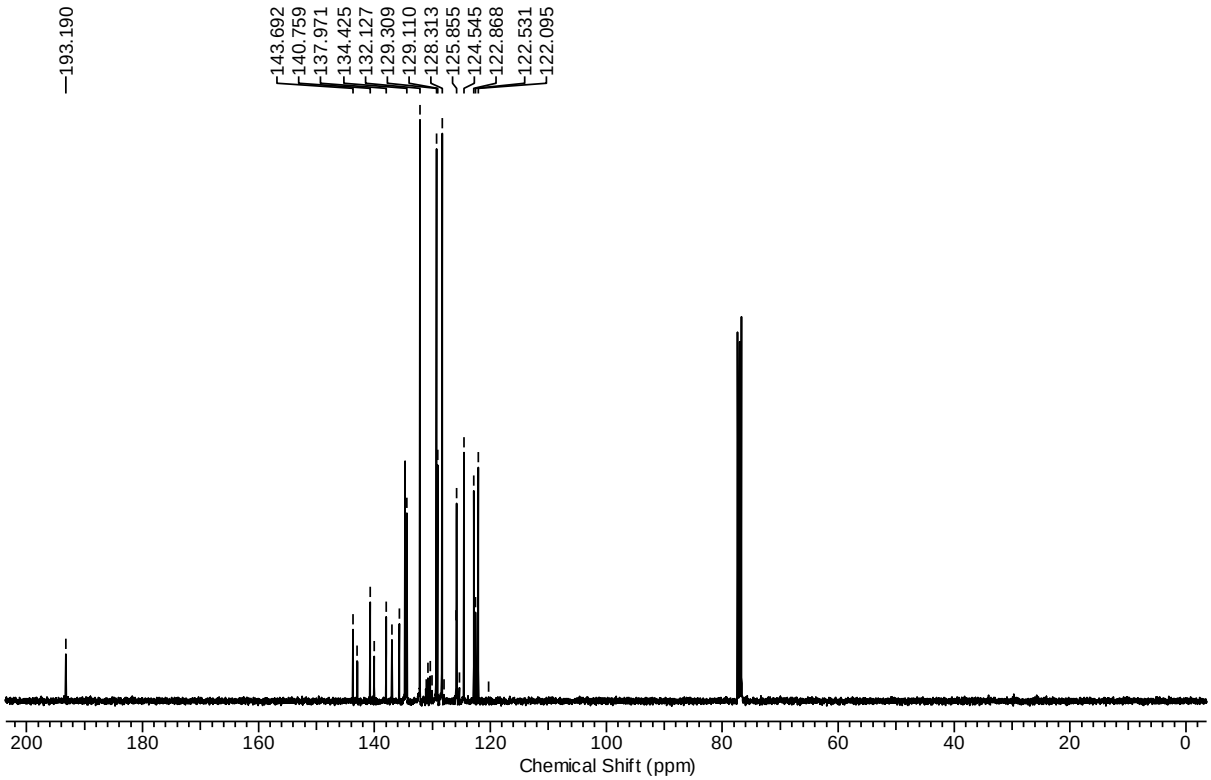


2,4-Bis(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8c)

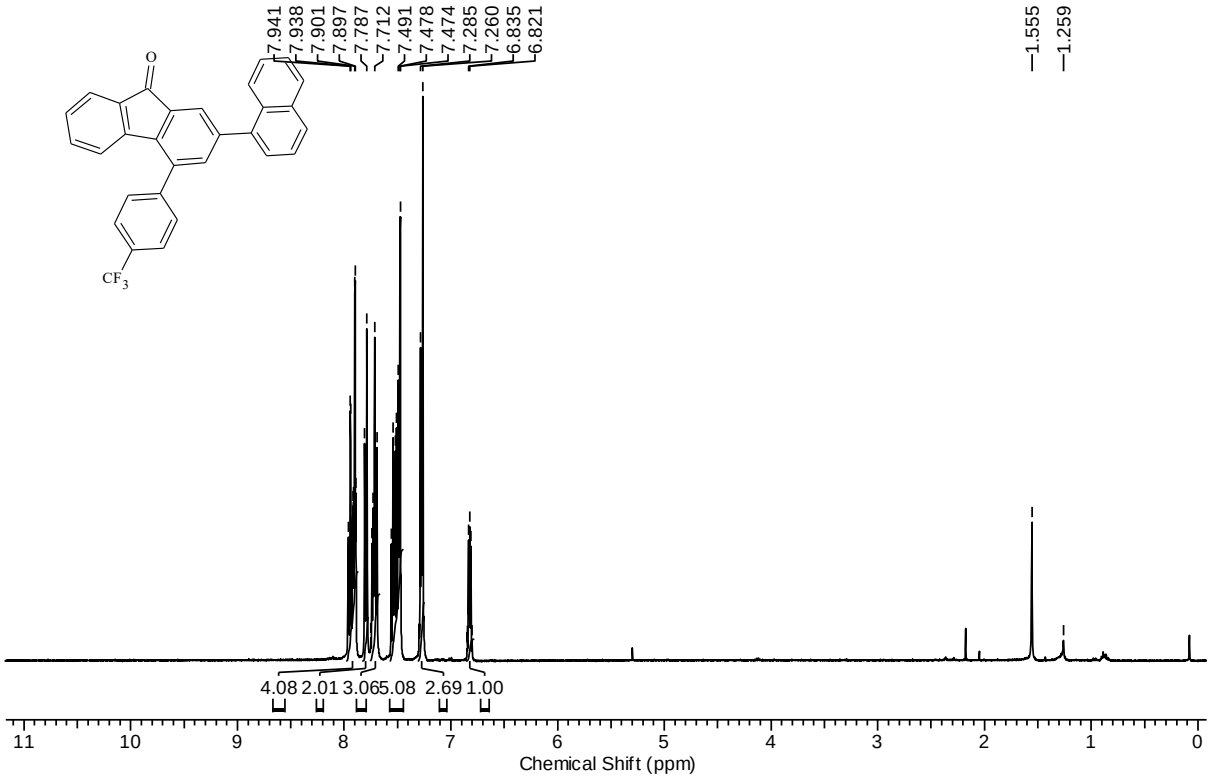


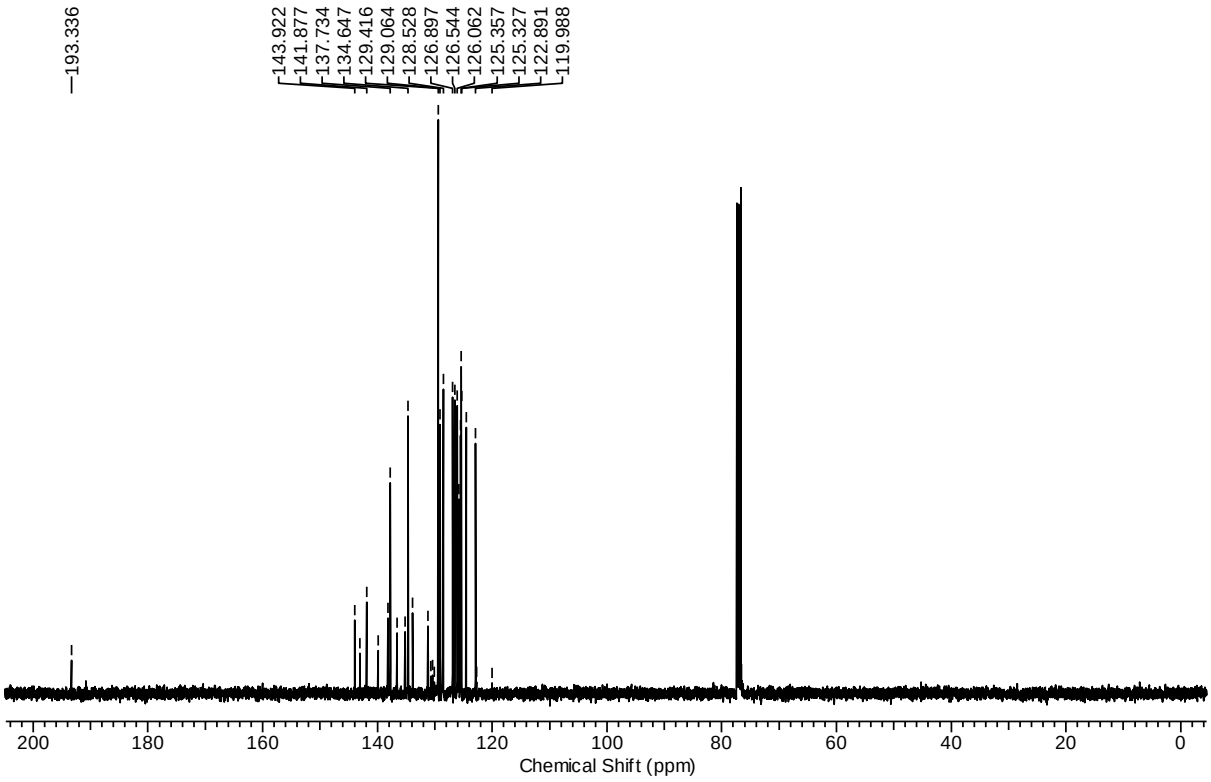
2-(4-Bromophenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8d)



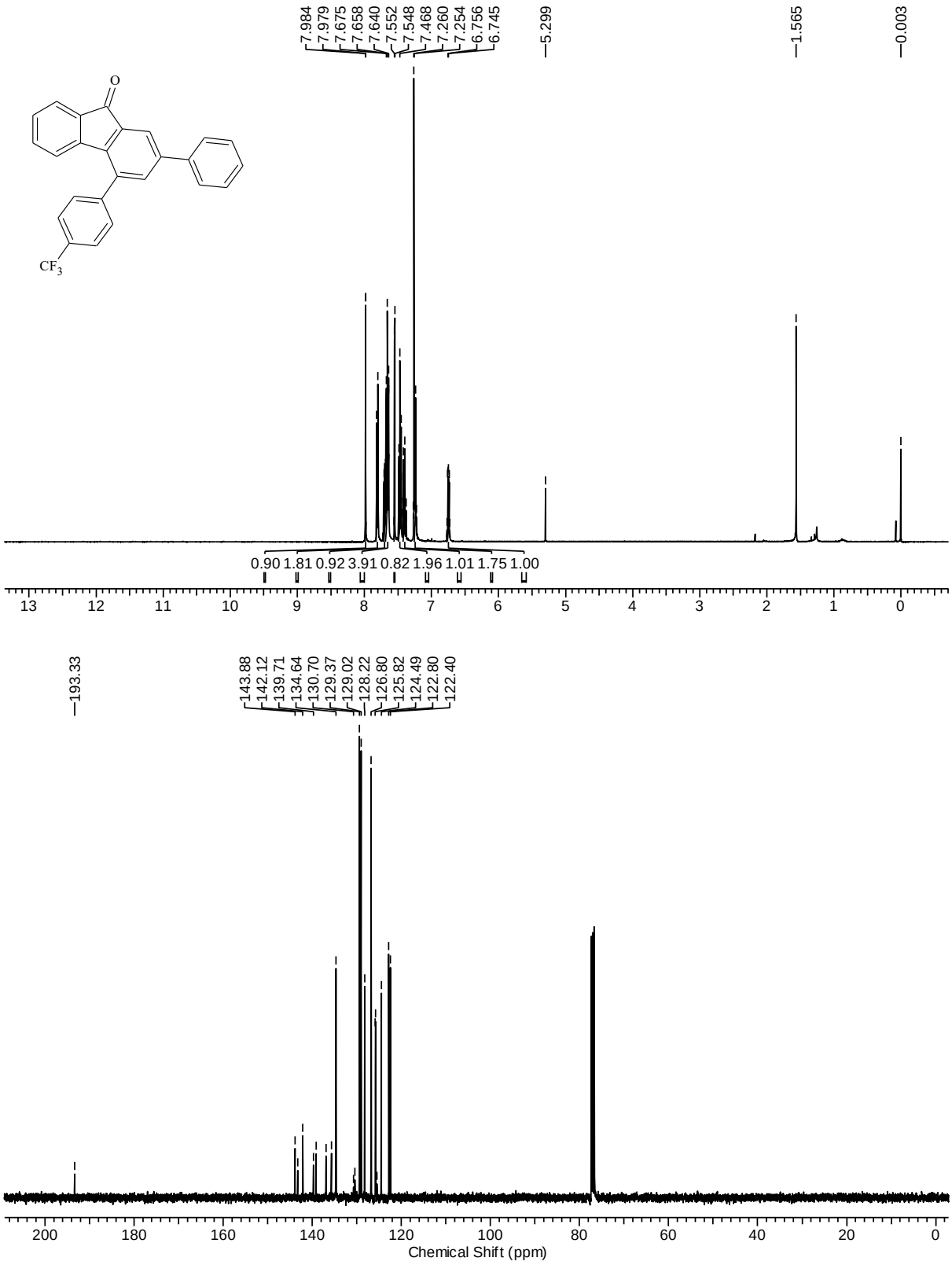


2-(Naphth-1-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8e)

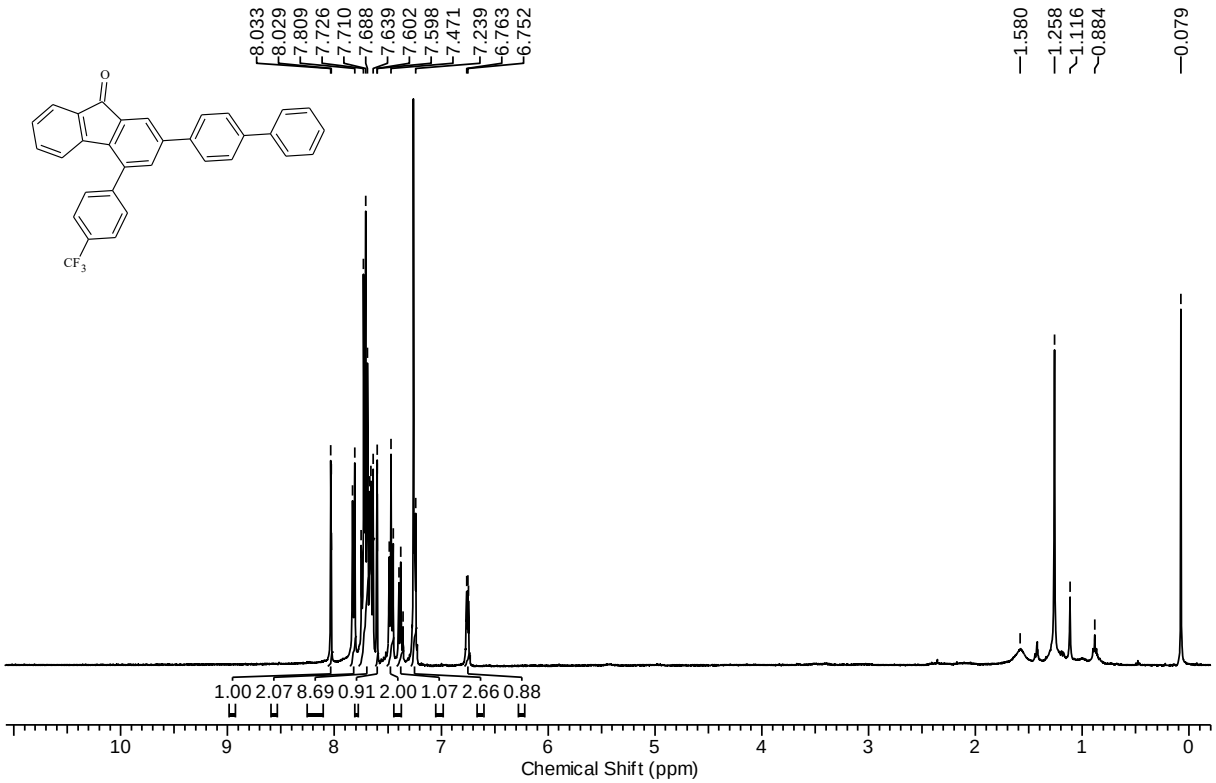


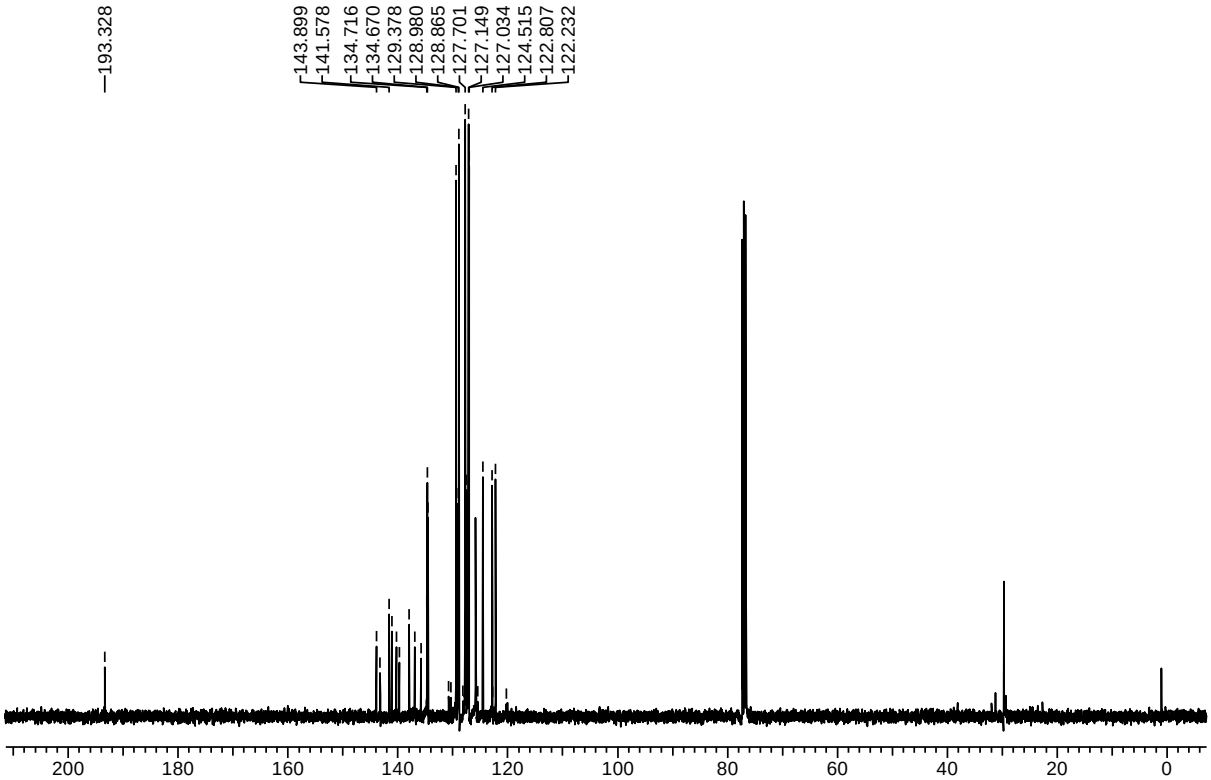


2-Phenyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8f)

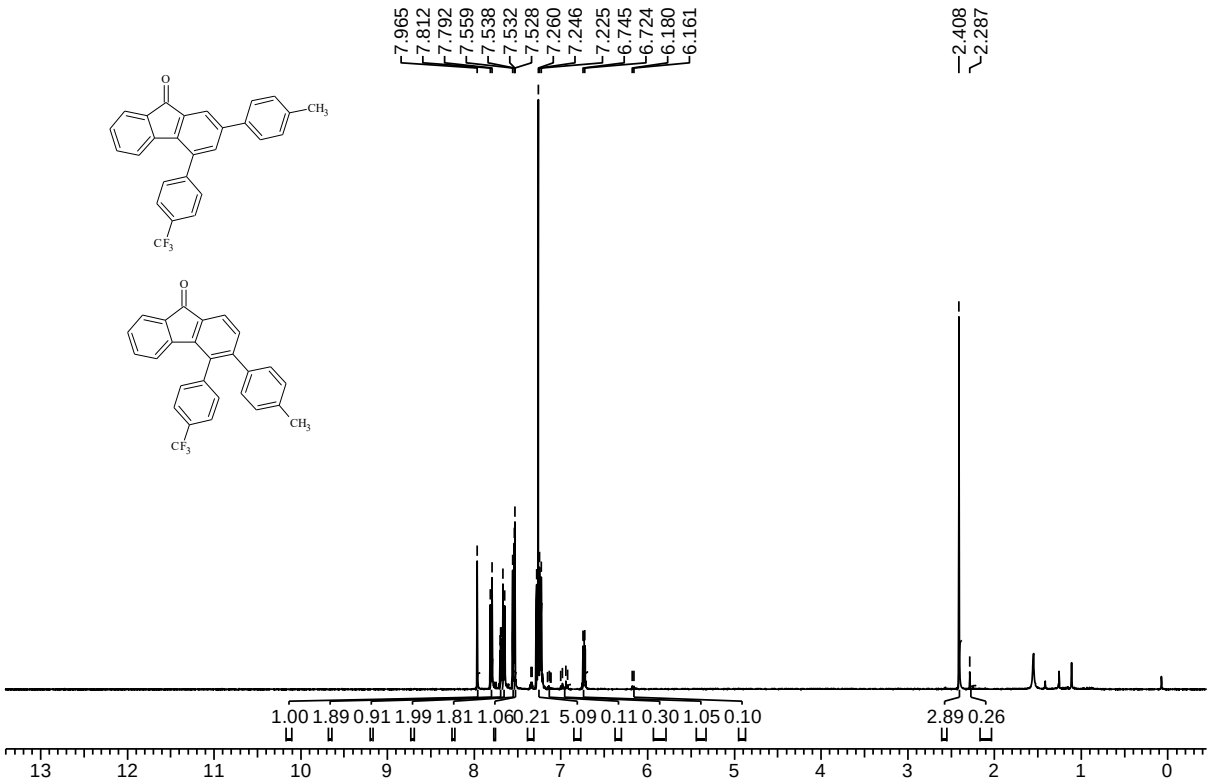


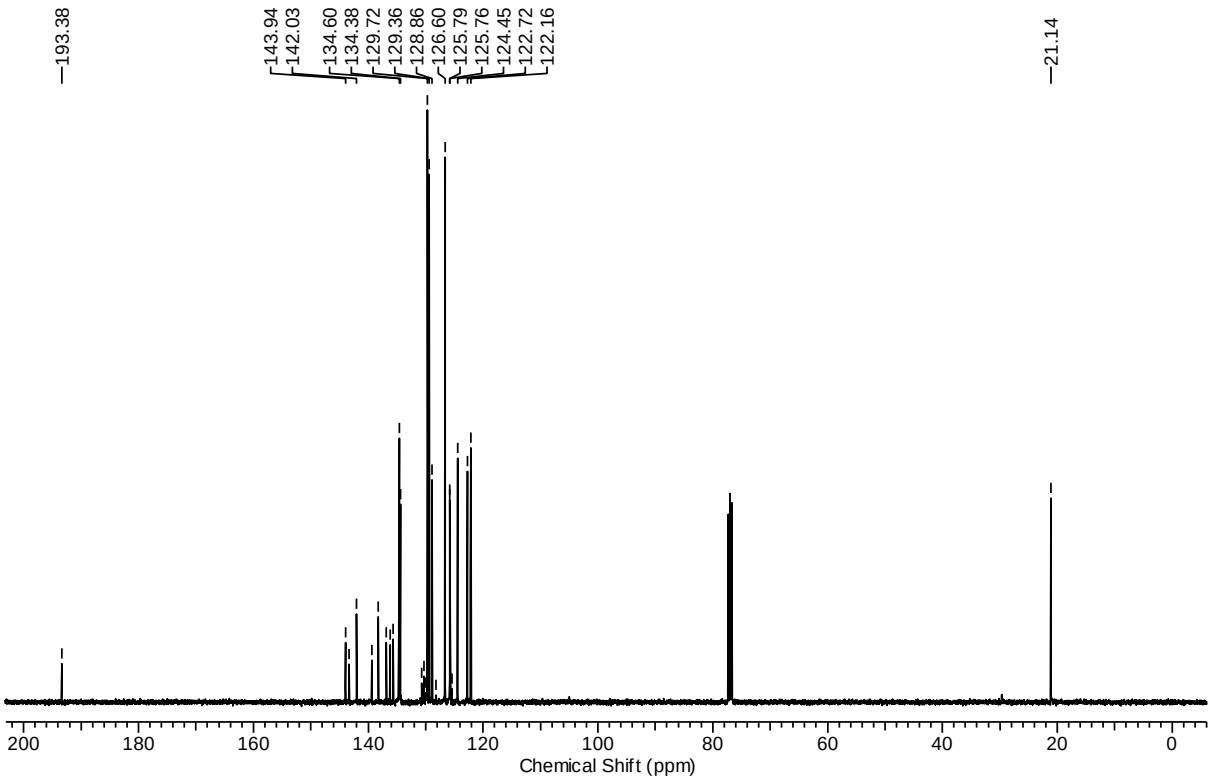
2-([1,1'-Biphenyl]-4-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8g)



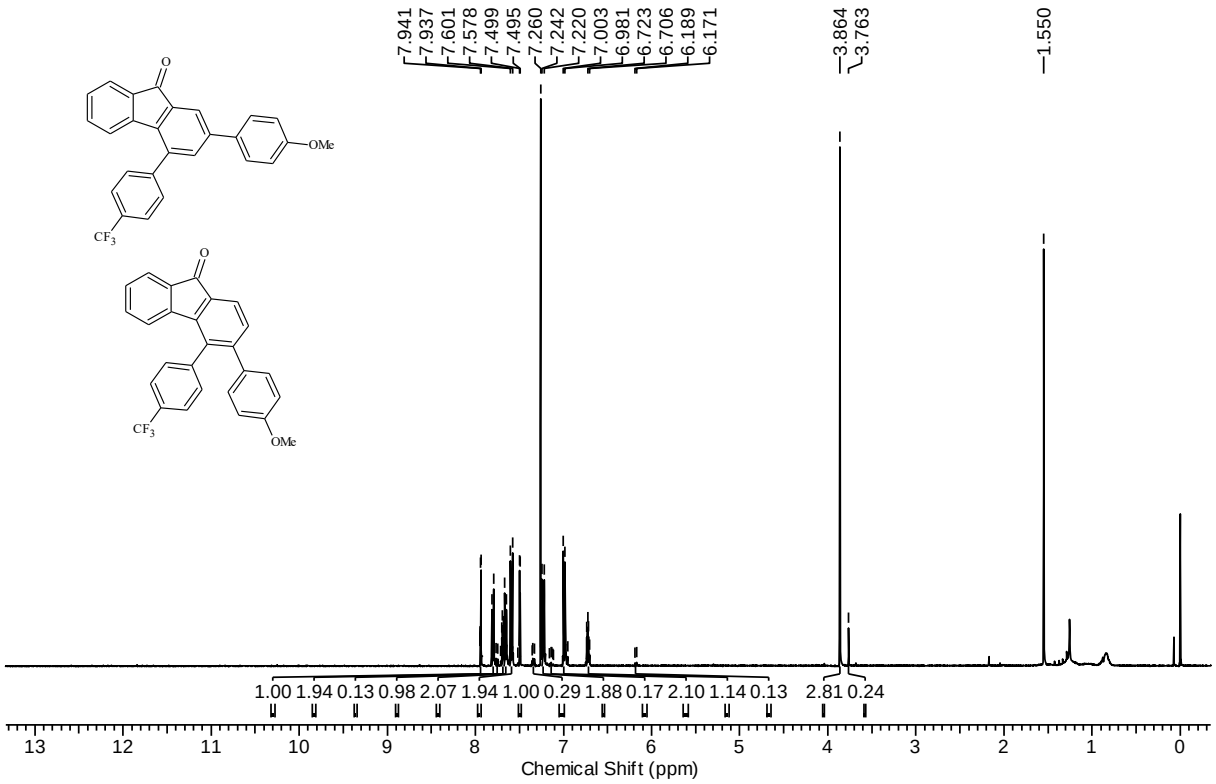


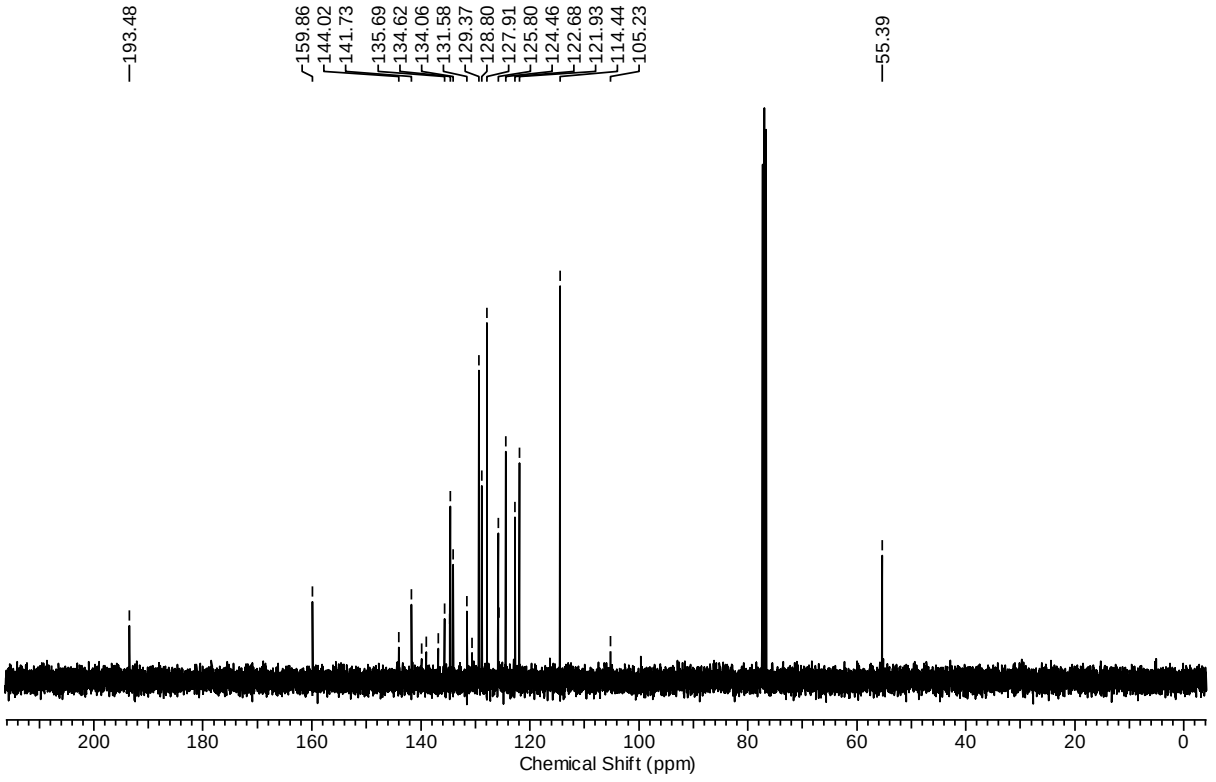
2-(*p*-Tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8h)



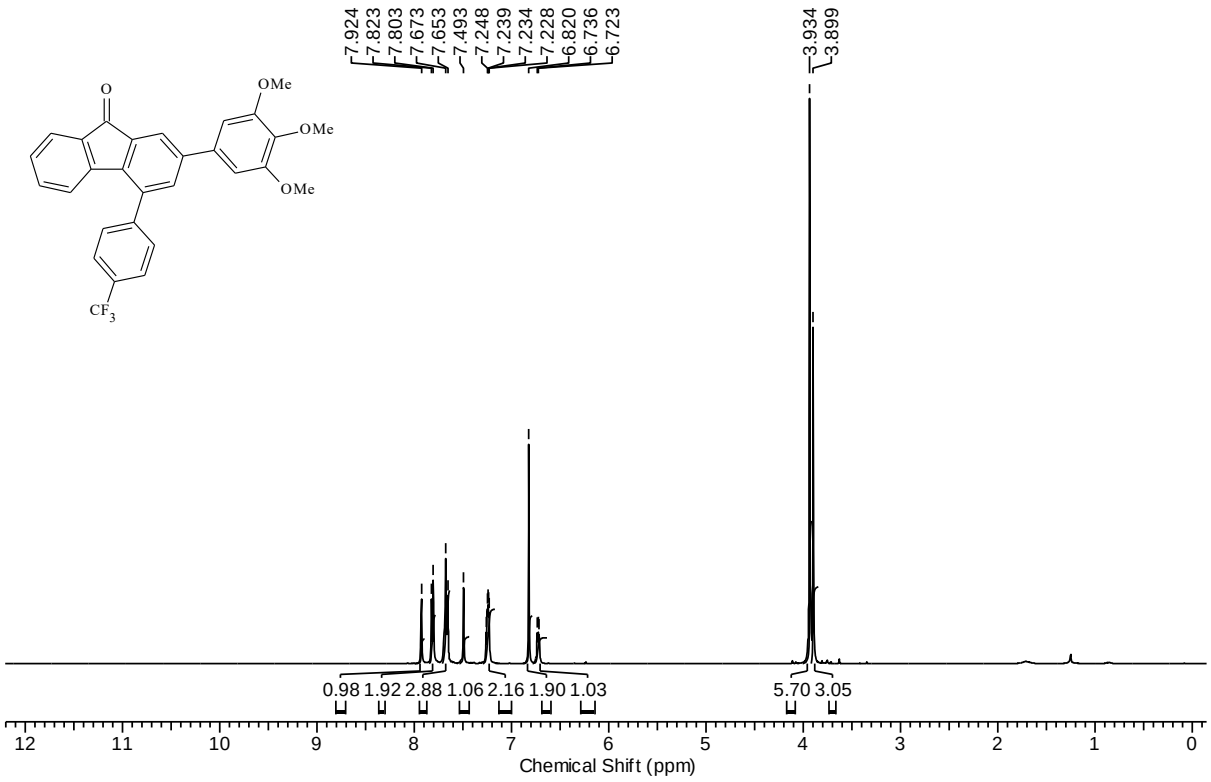


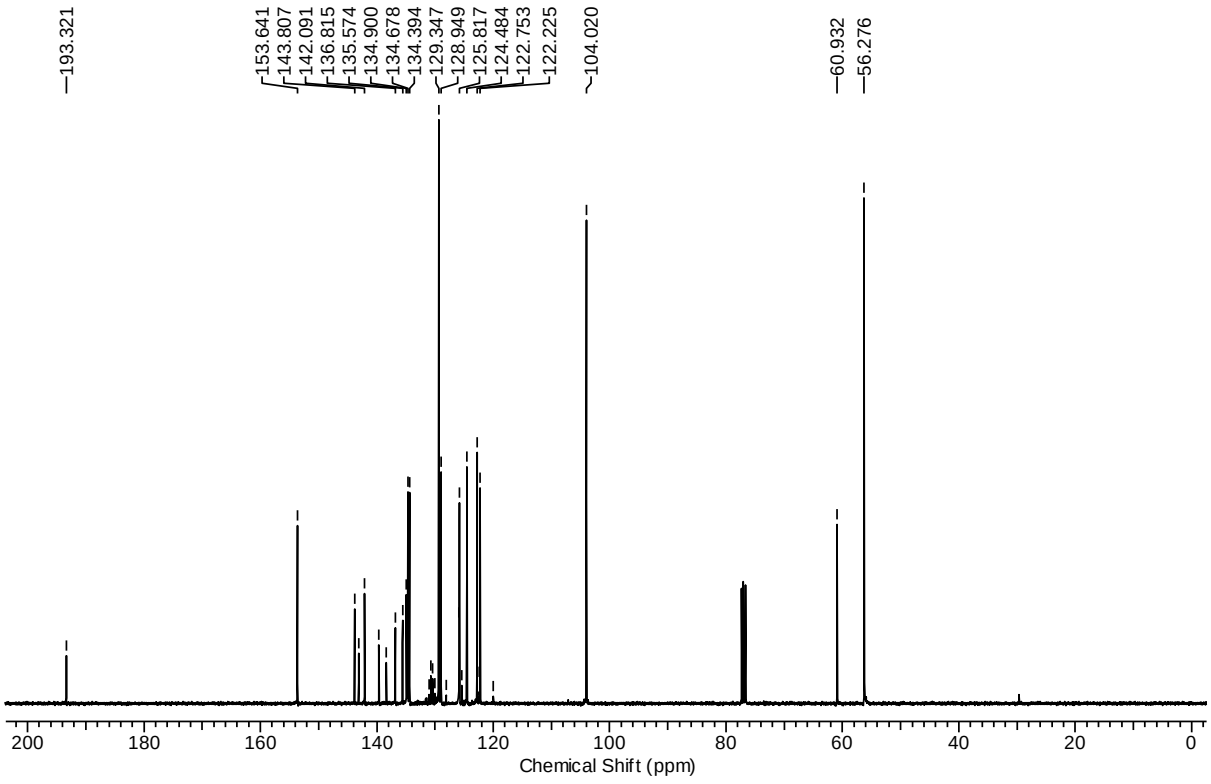
2-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8i)



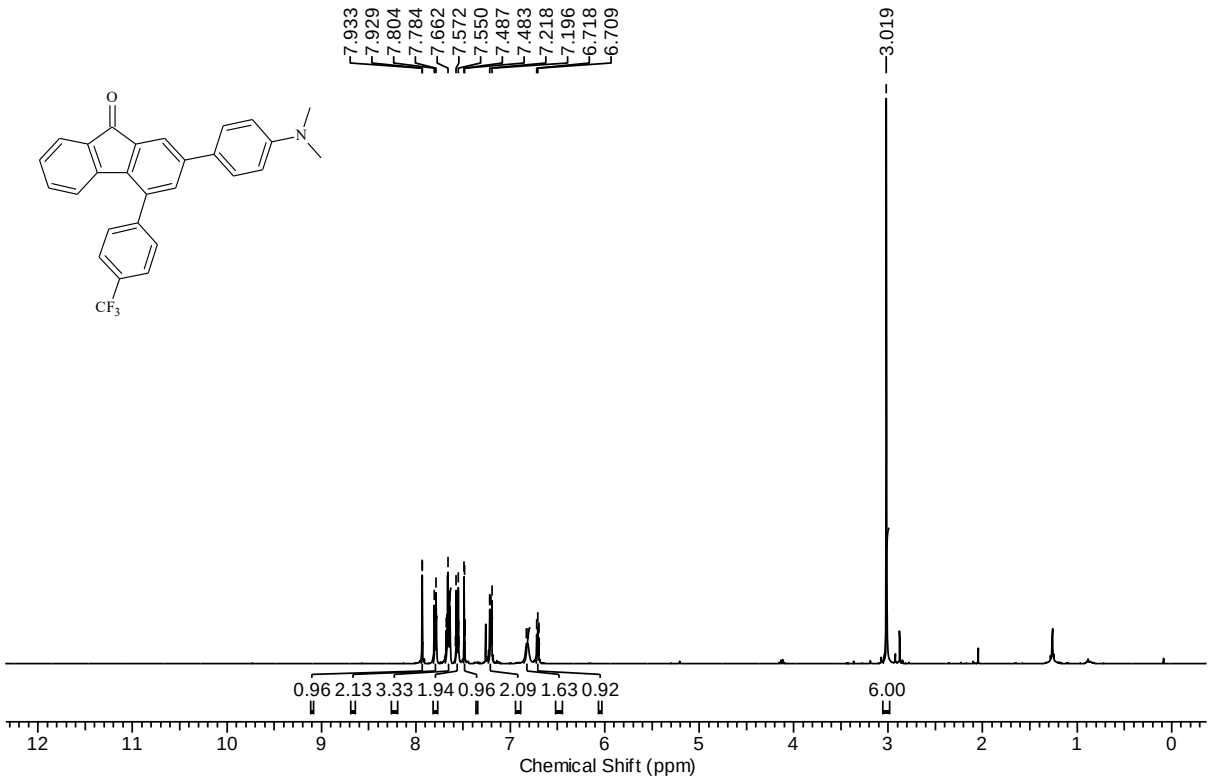


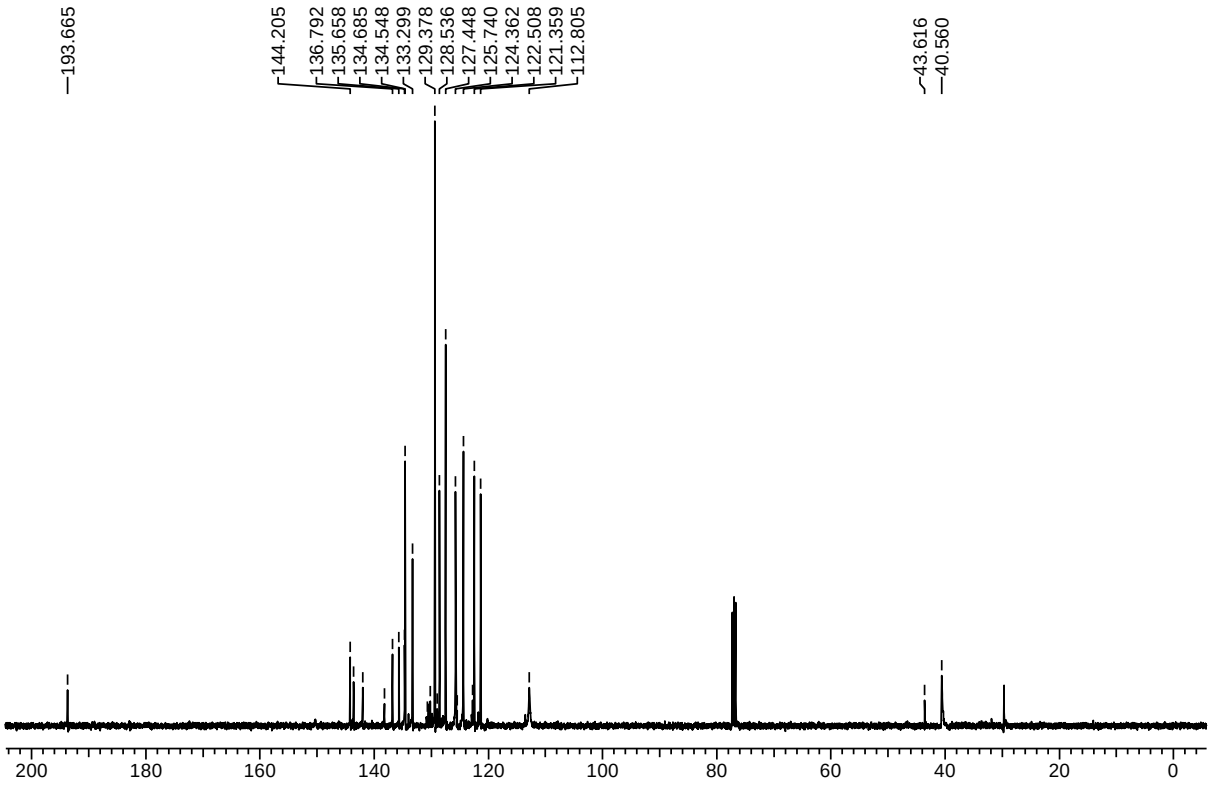
4-(4-(Trifluoromethyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-9*H*-fluoren-9-one (8j)



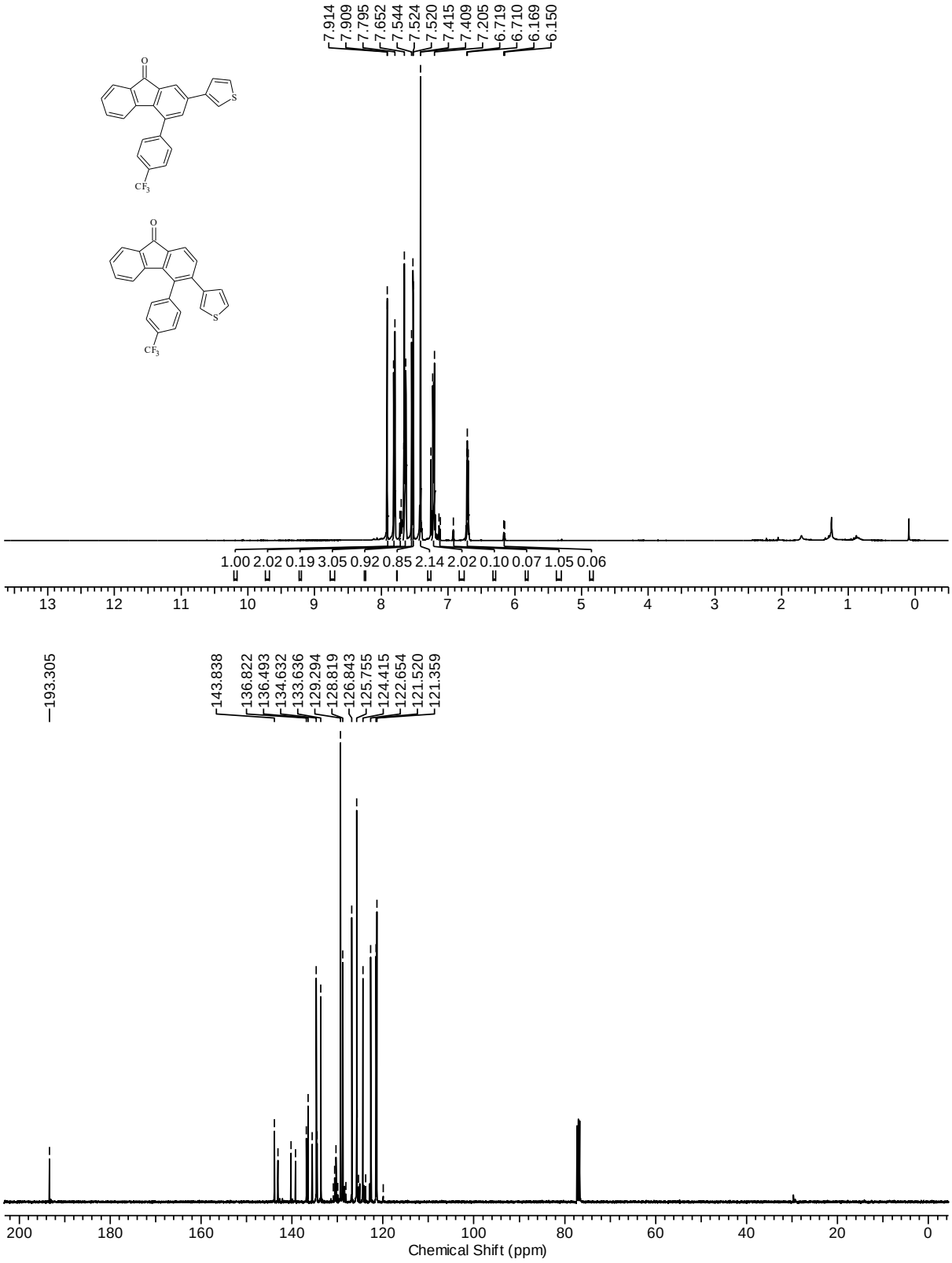


2-(4-(*N*,*N*-Dimethylamino)phenyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8k)

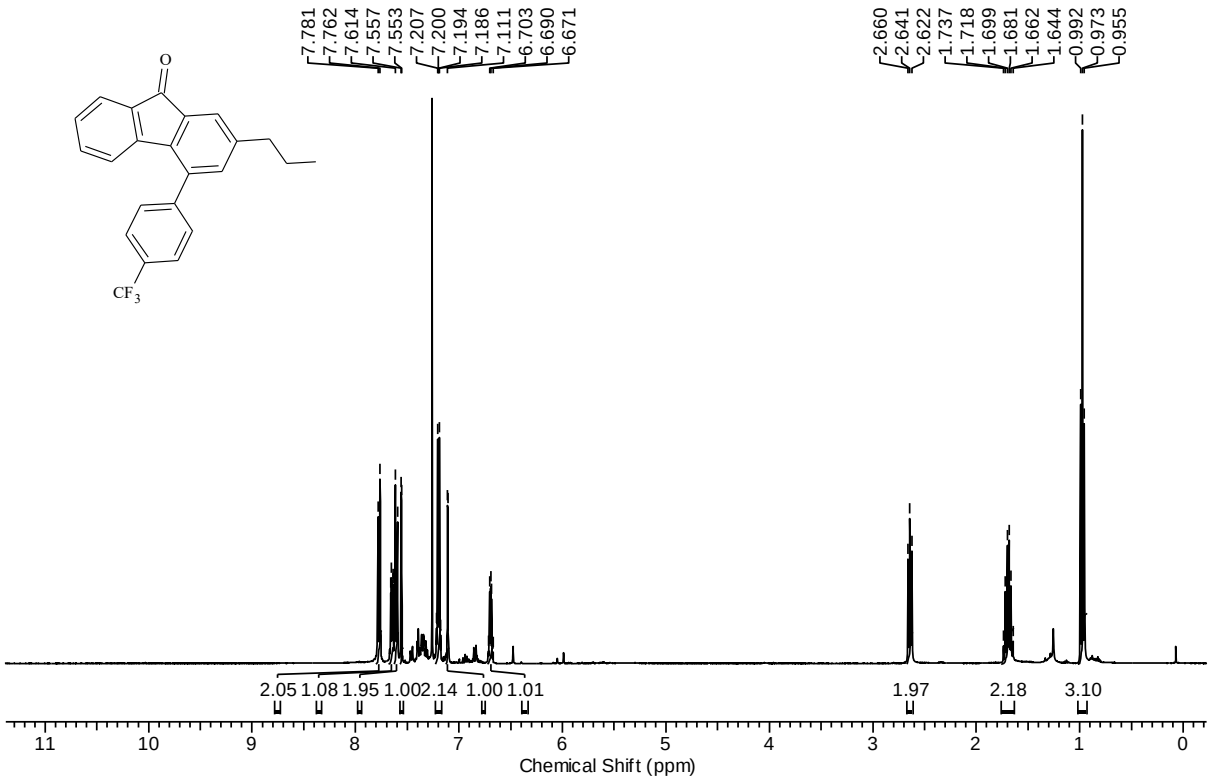


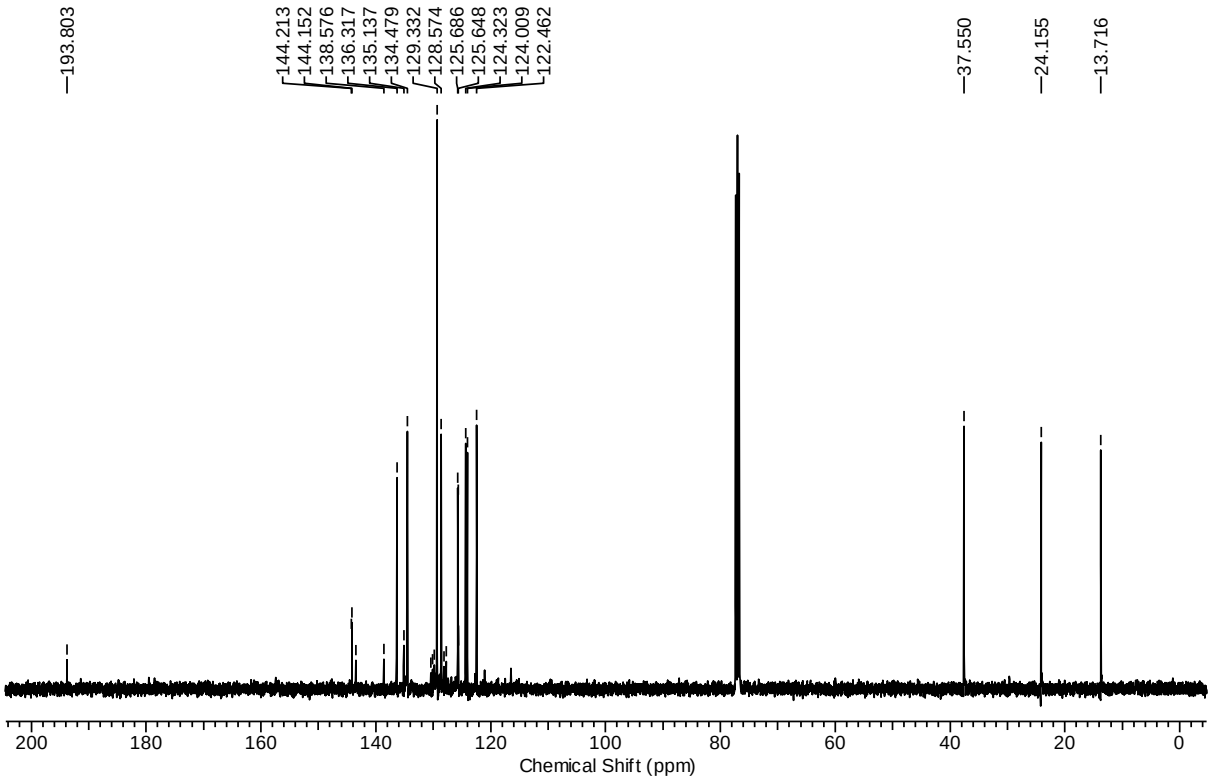


2-(Thien-3-yl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8l)

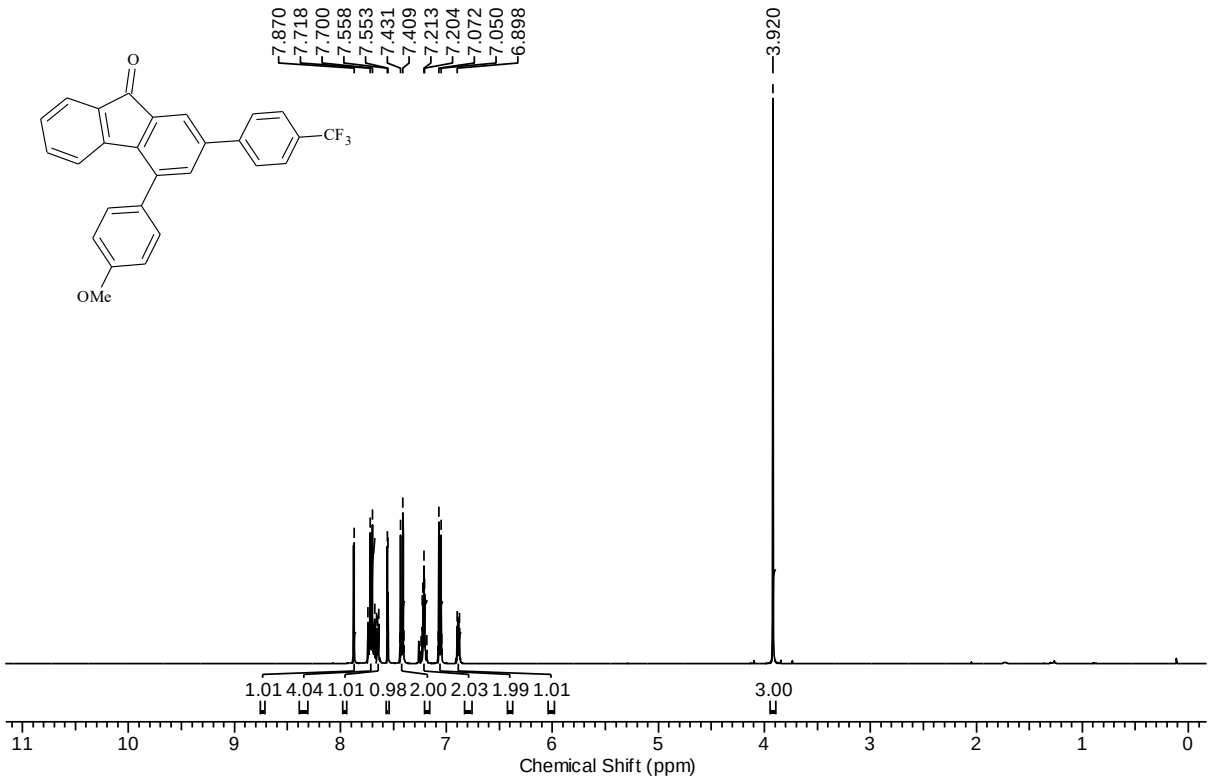


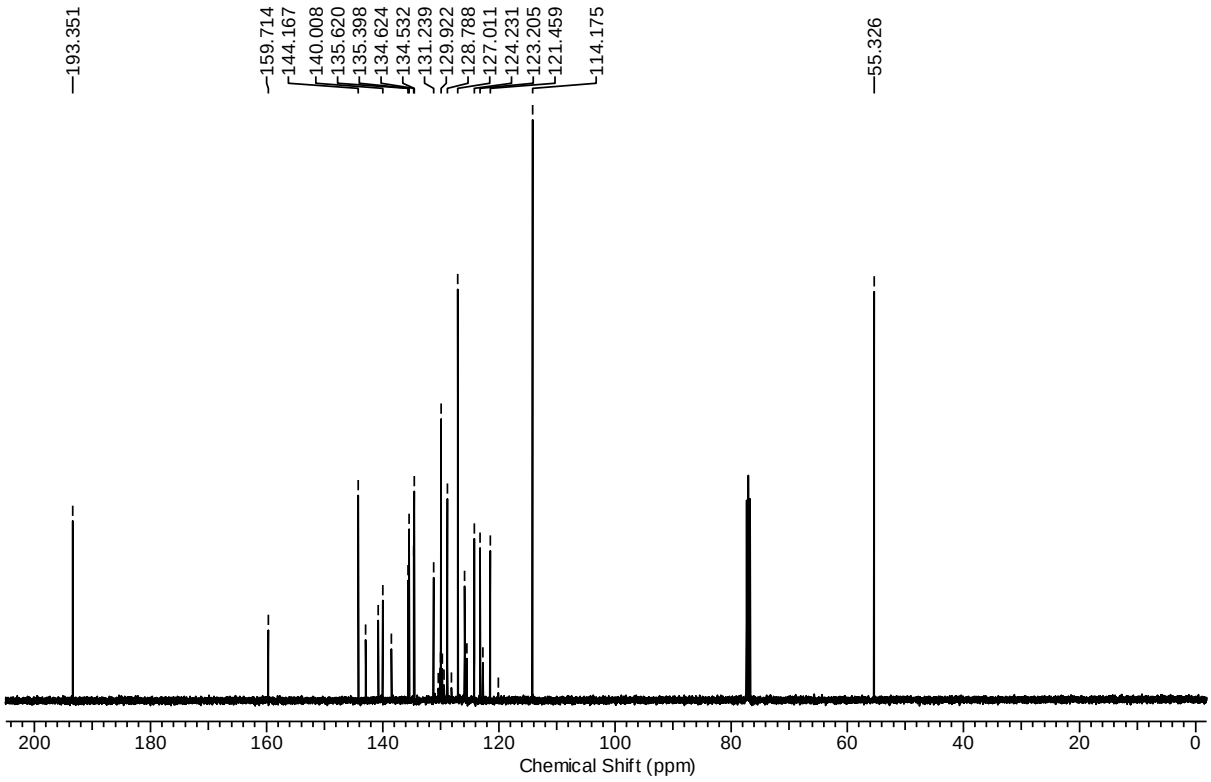
2-Propyl-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8m)



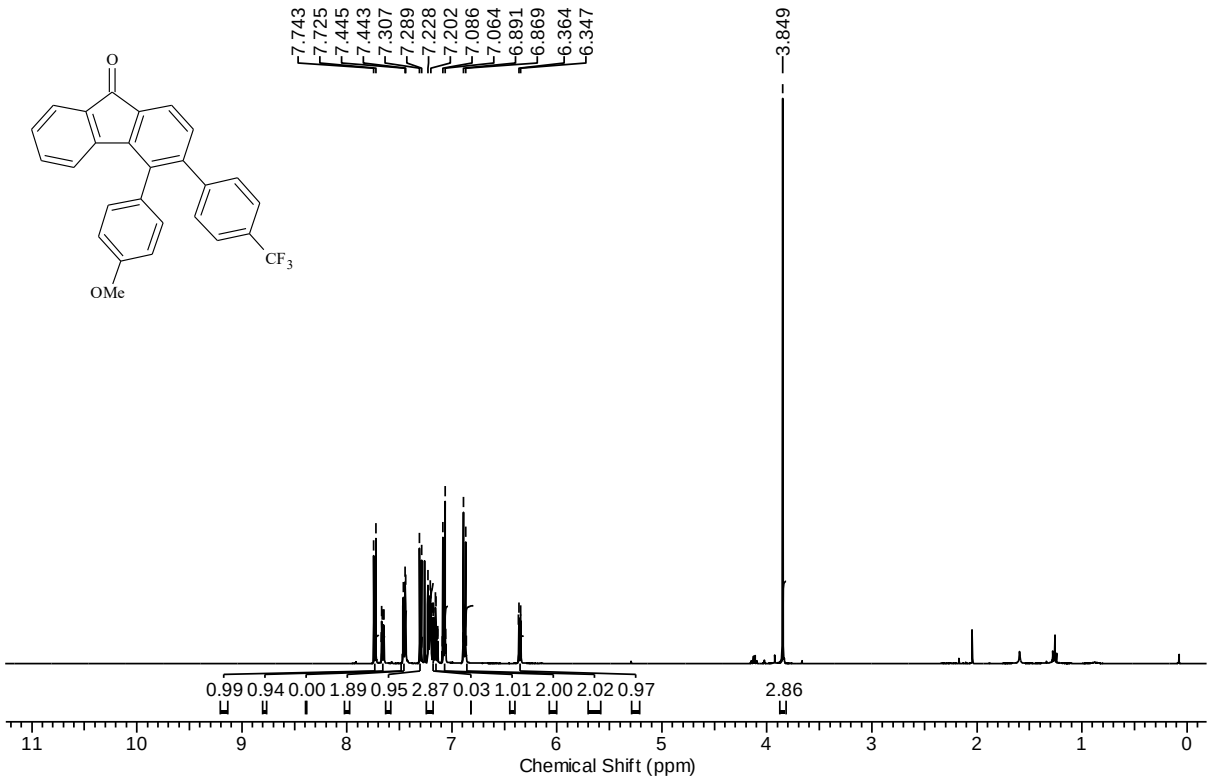


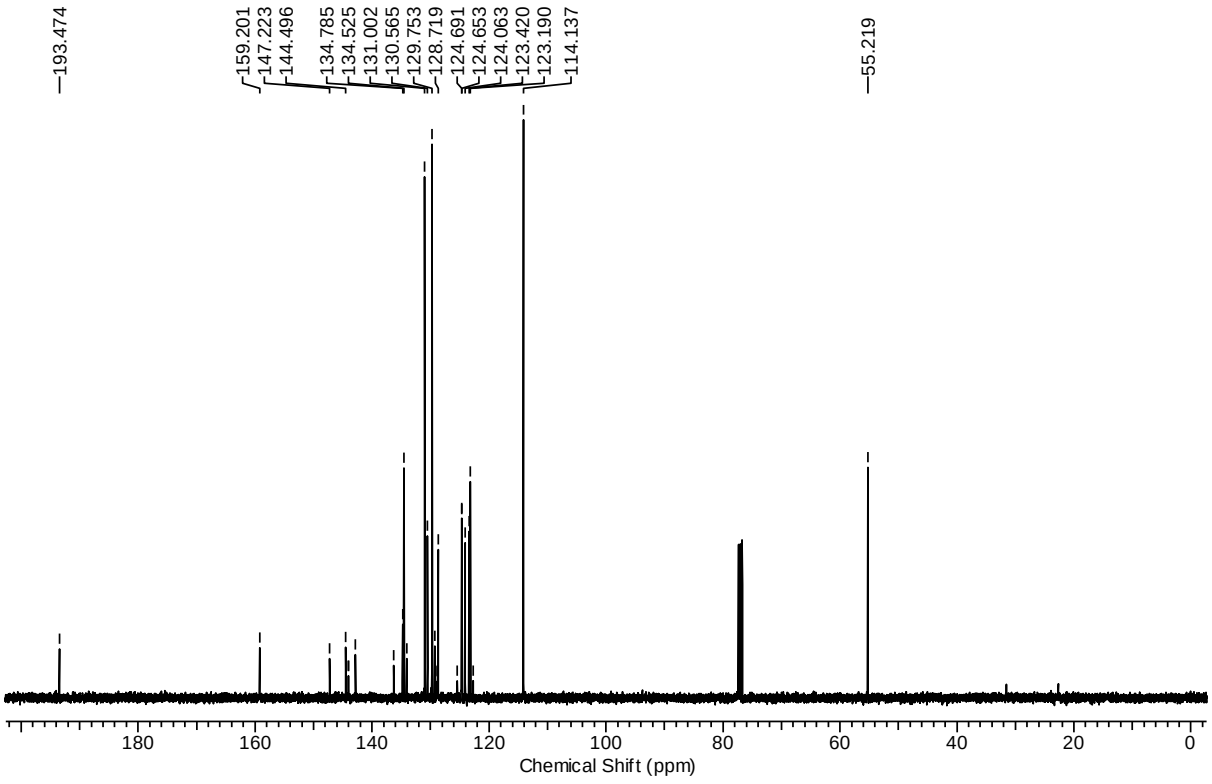
4-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8n)



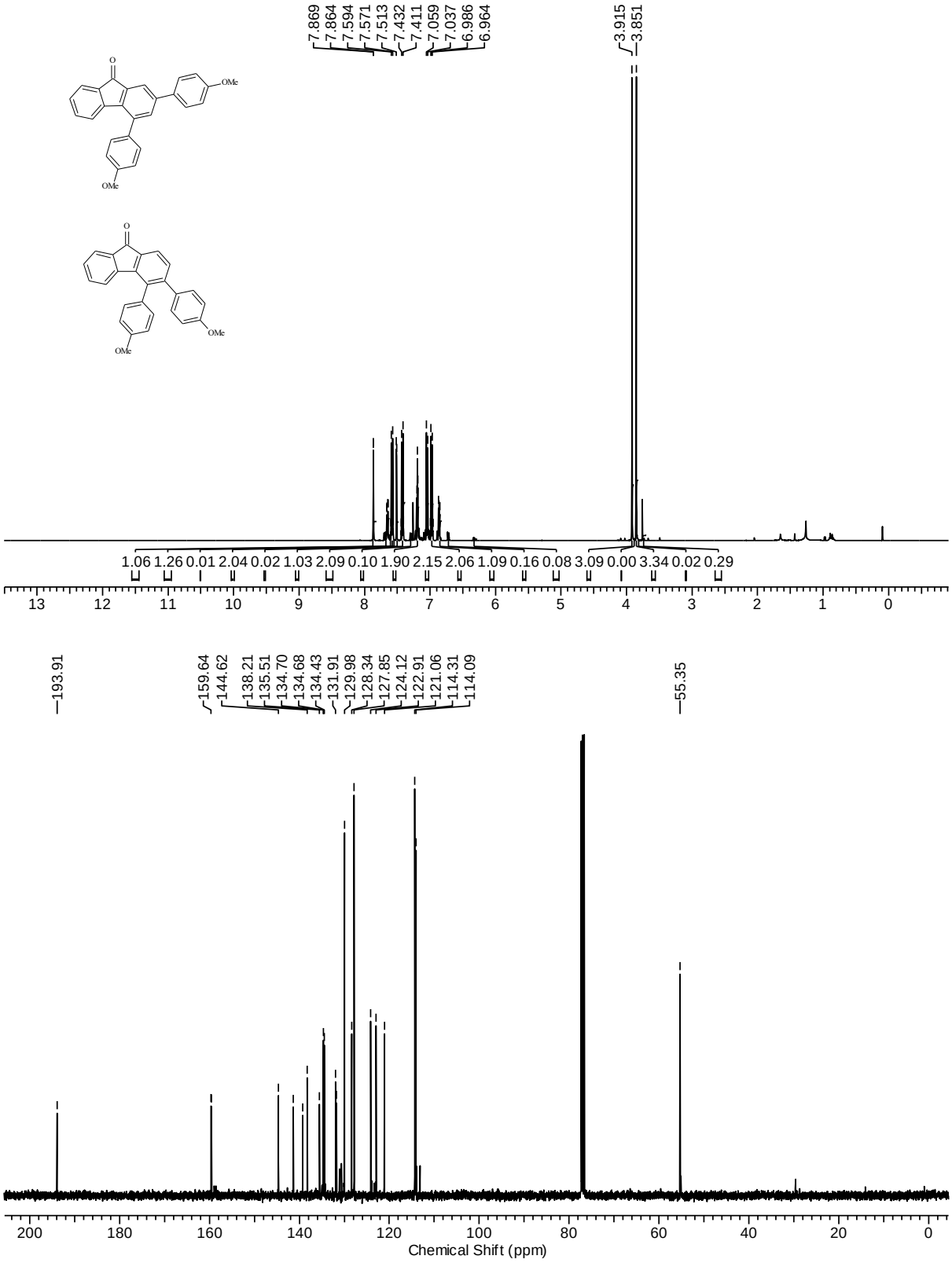


4-(4-Methoxyphenyl)-3-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (8n')

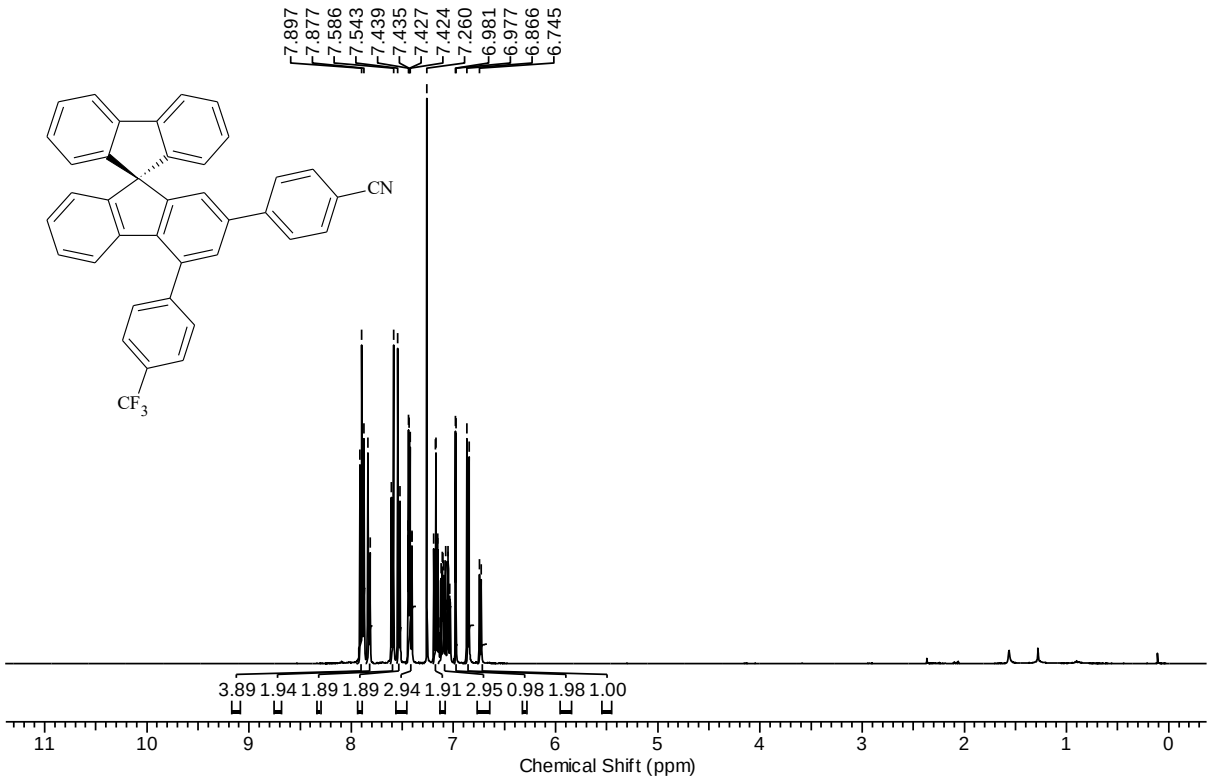


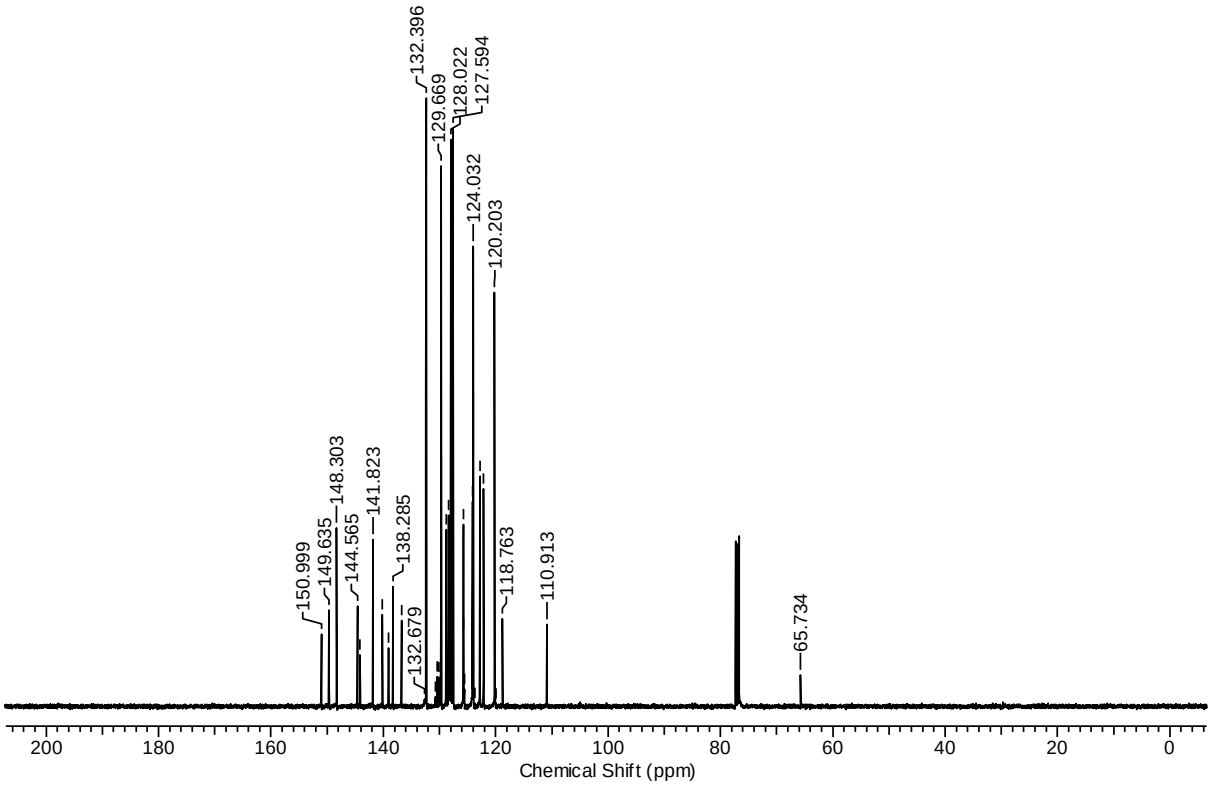


2,4-Bis(4-methoxyphenyl)-9*H*-fluoren-9-one (8o)

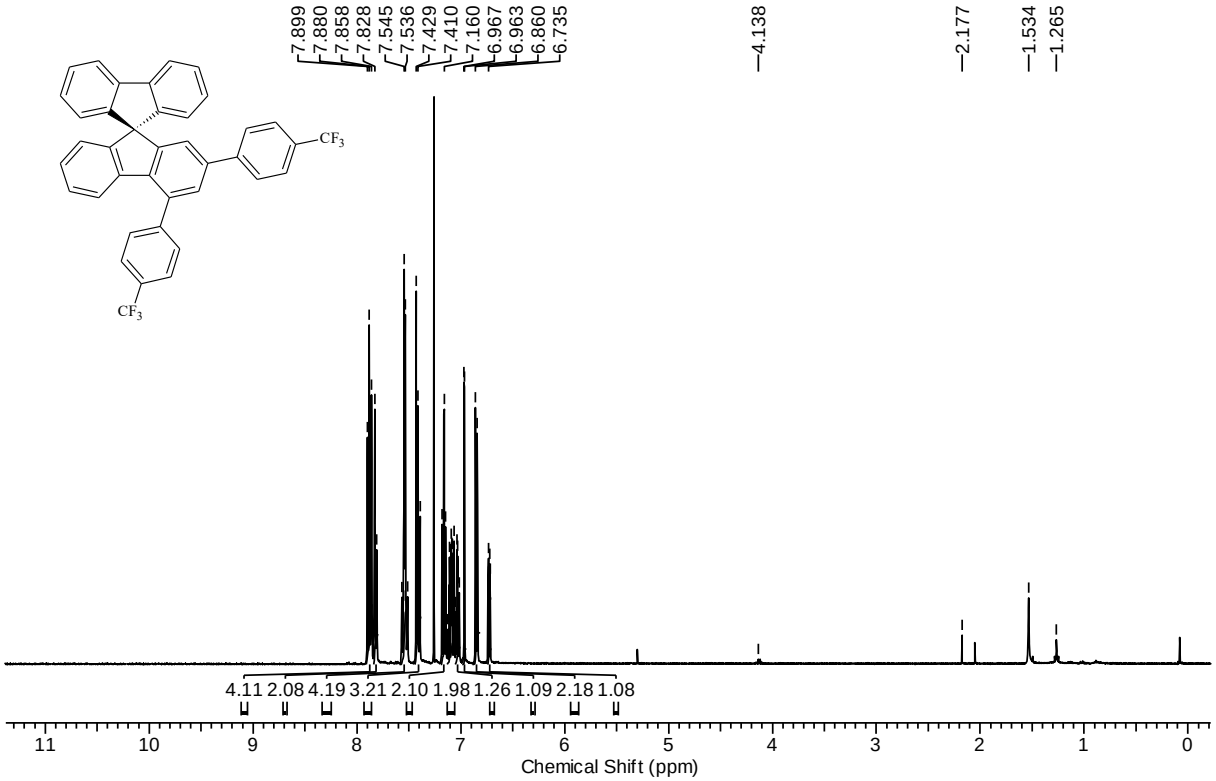


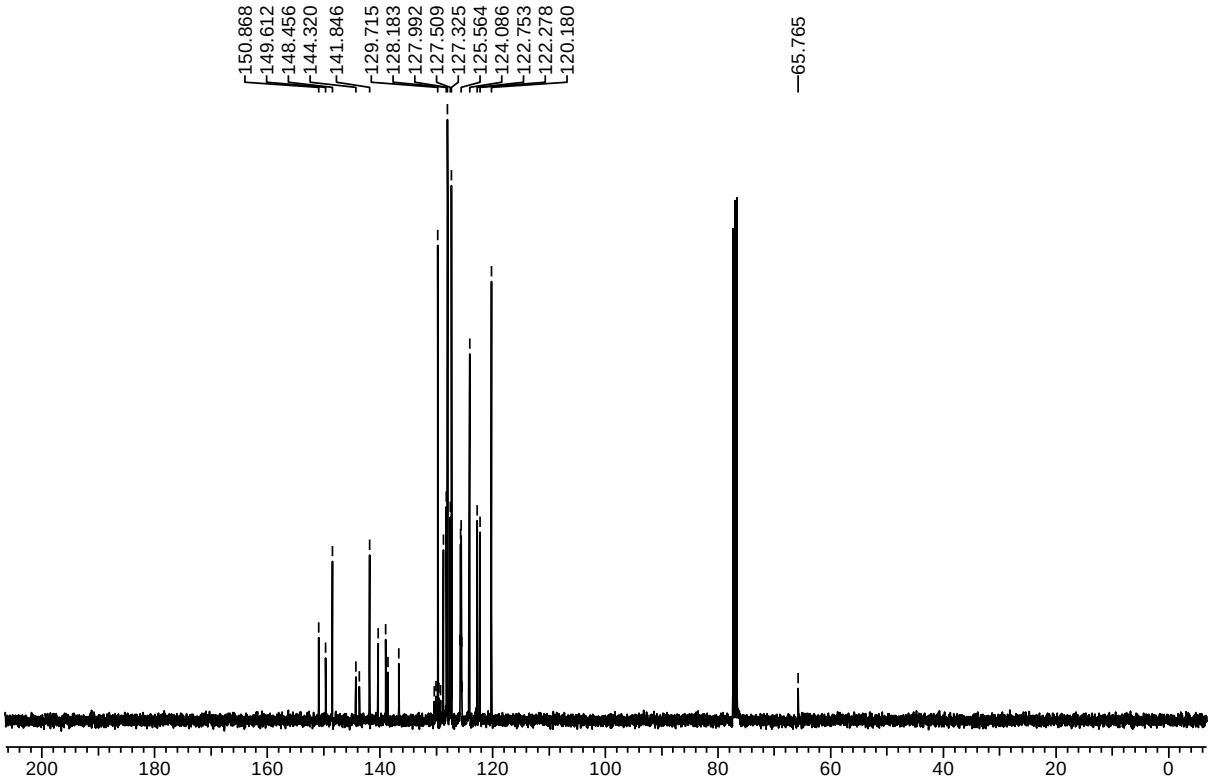
4-(4-(4-(Trifluoromethyl)phenyl)-9,9'-spirobi[fluoren]-2-yl)benzonitrile (9b)



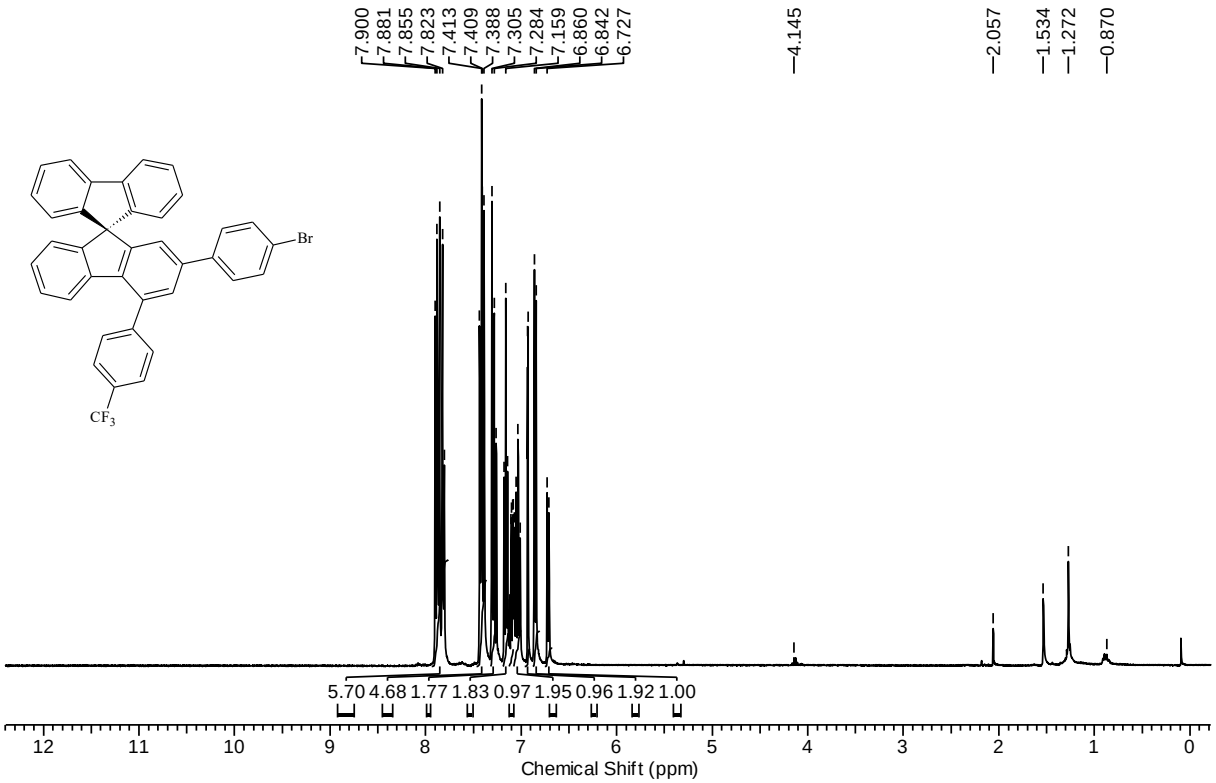


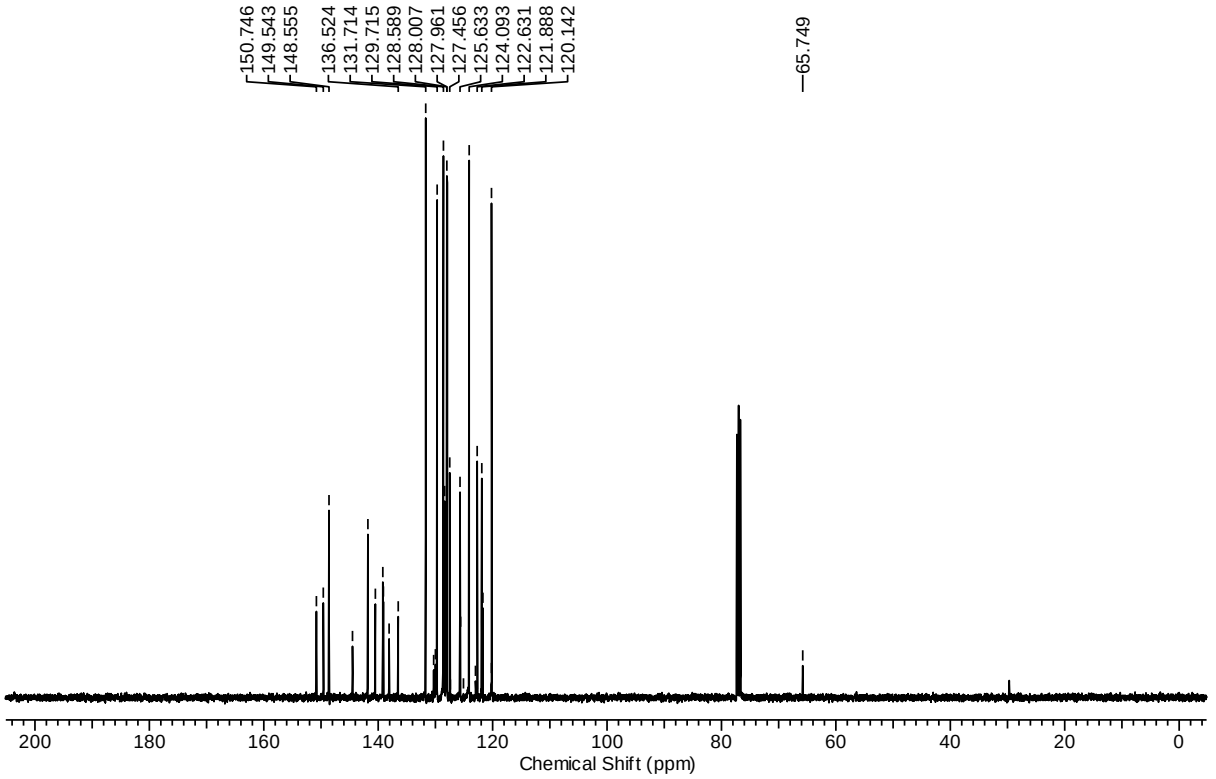
2,4-Bis(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9c)



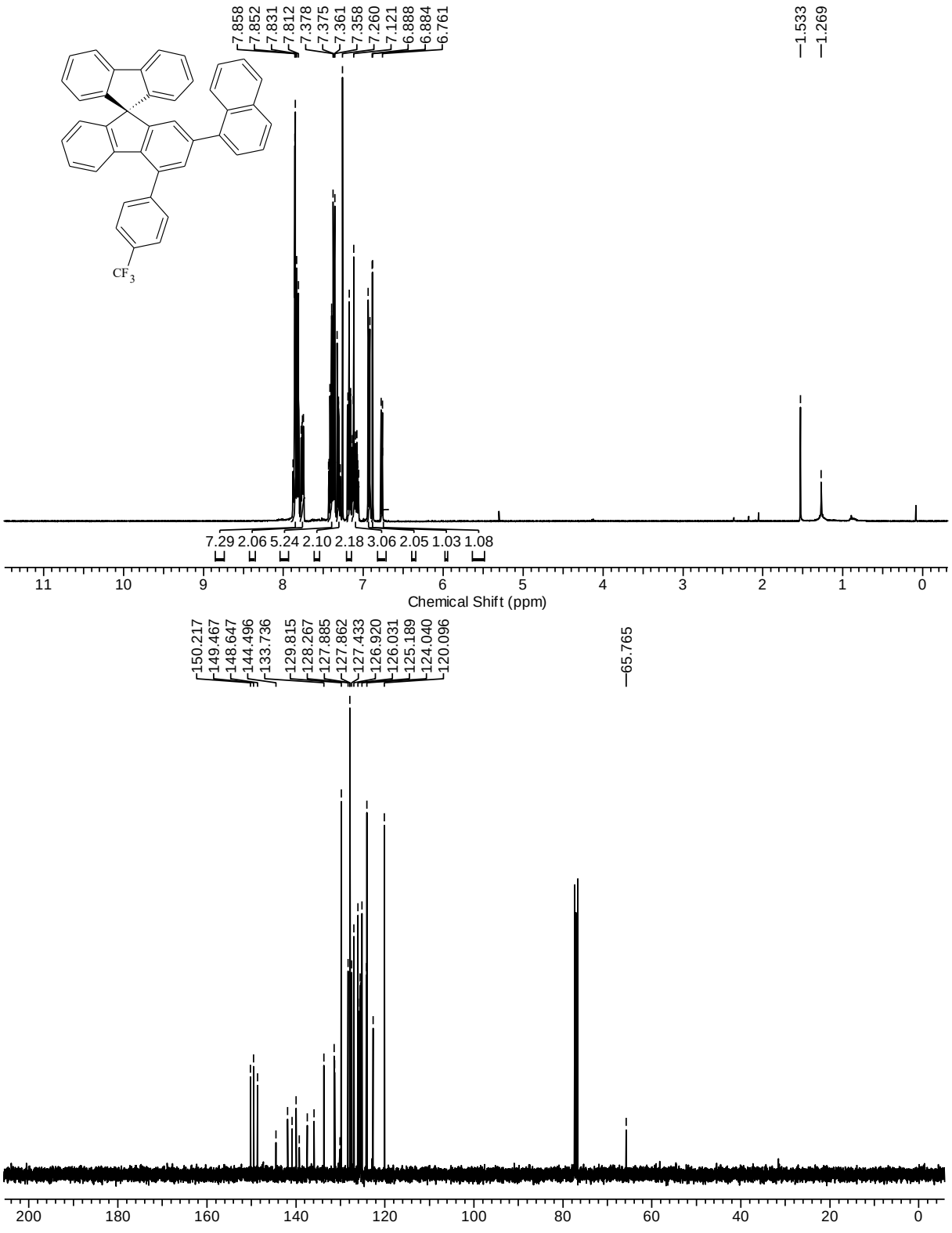


2-(4-Bromophenyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9d)

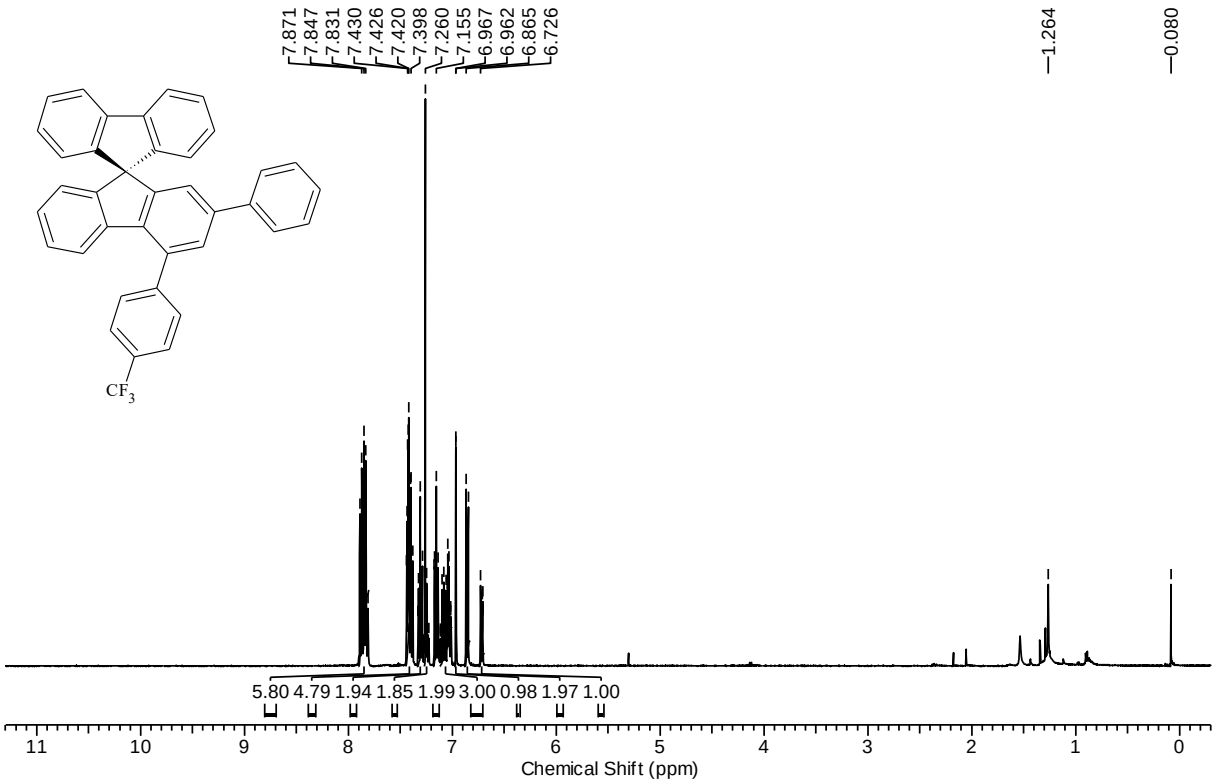


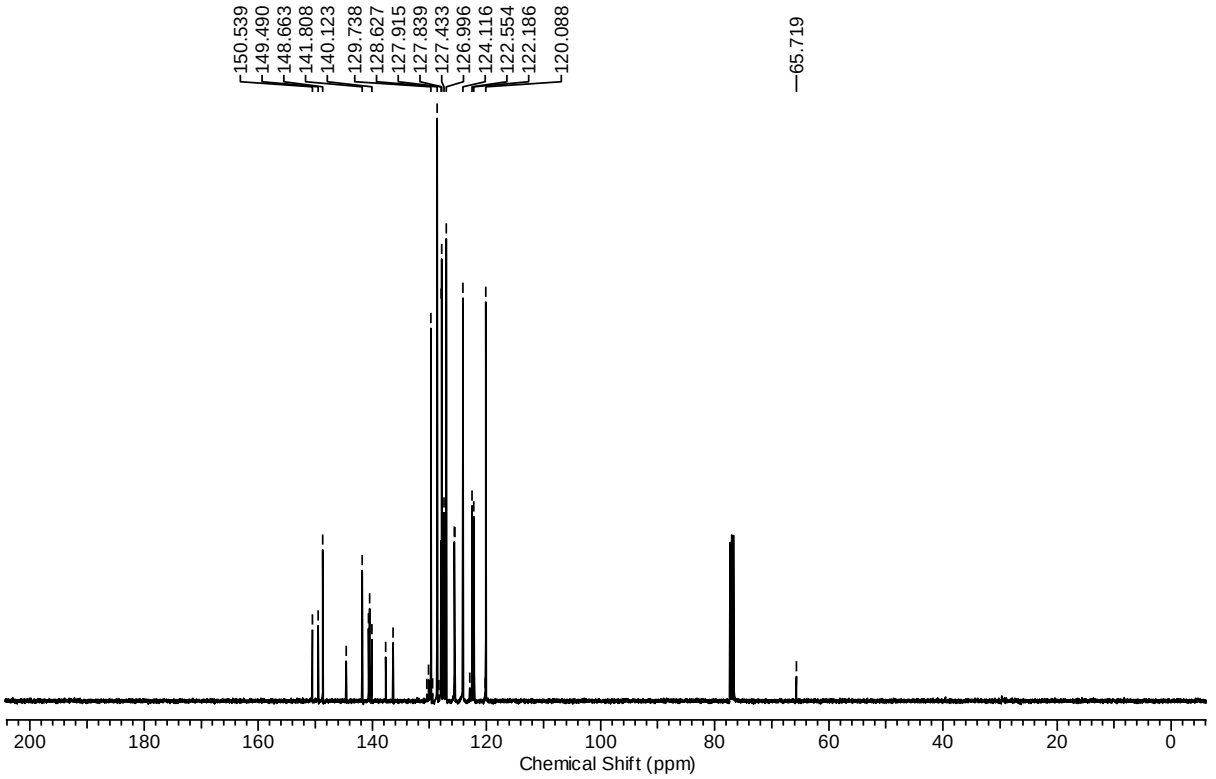


2-(Naphth-1-yl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9e)

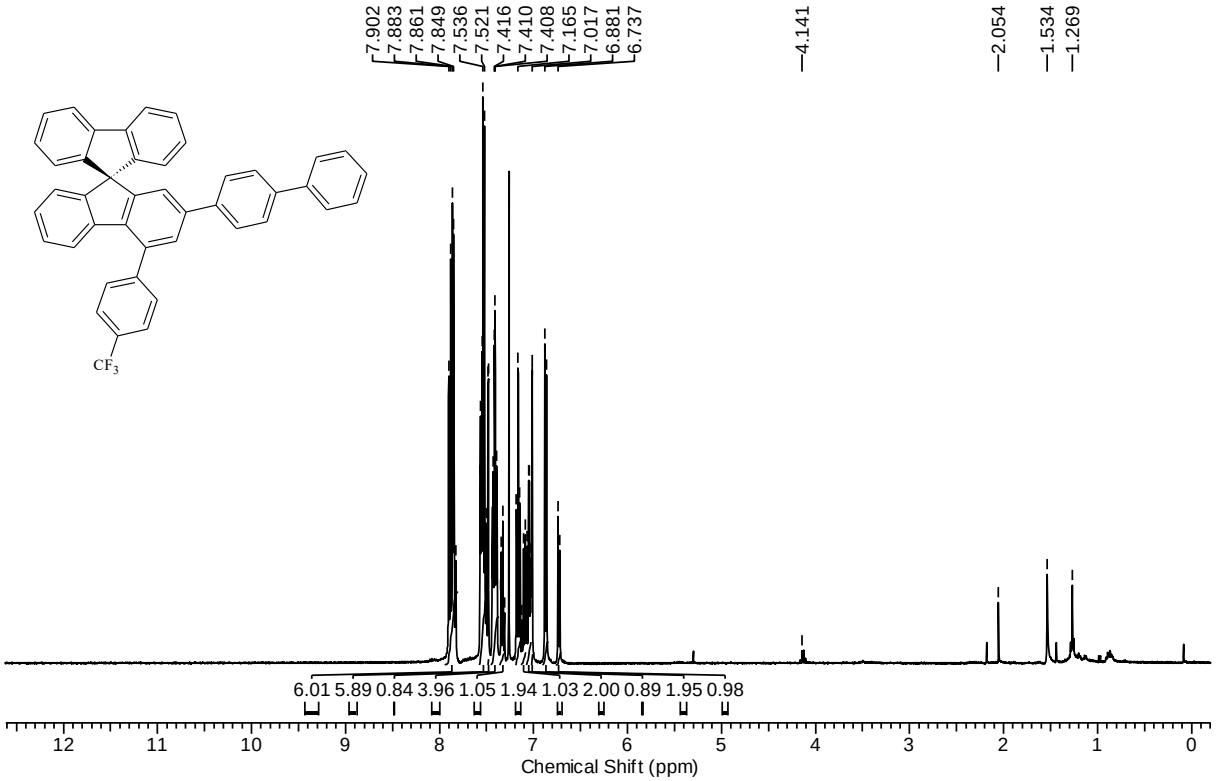


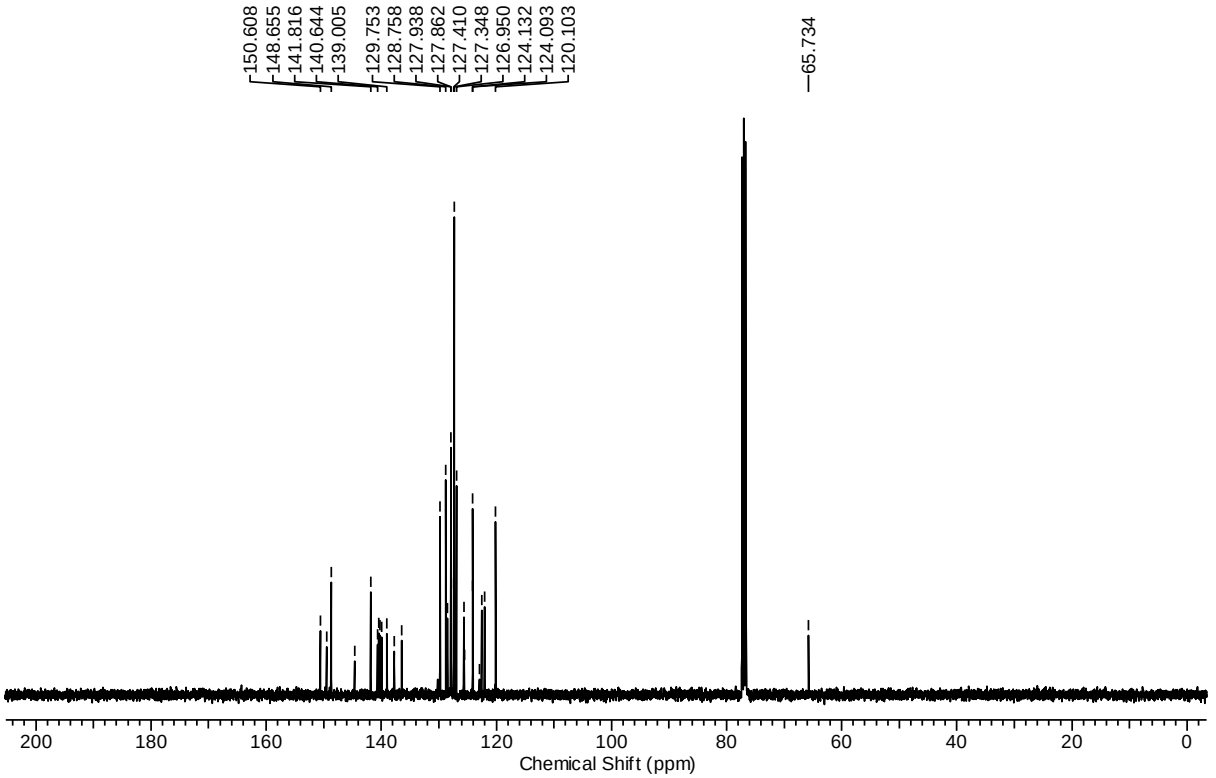
2-Phenyl-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9f)



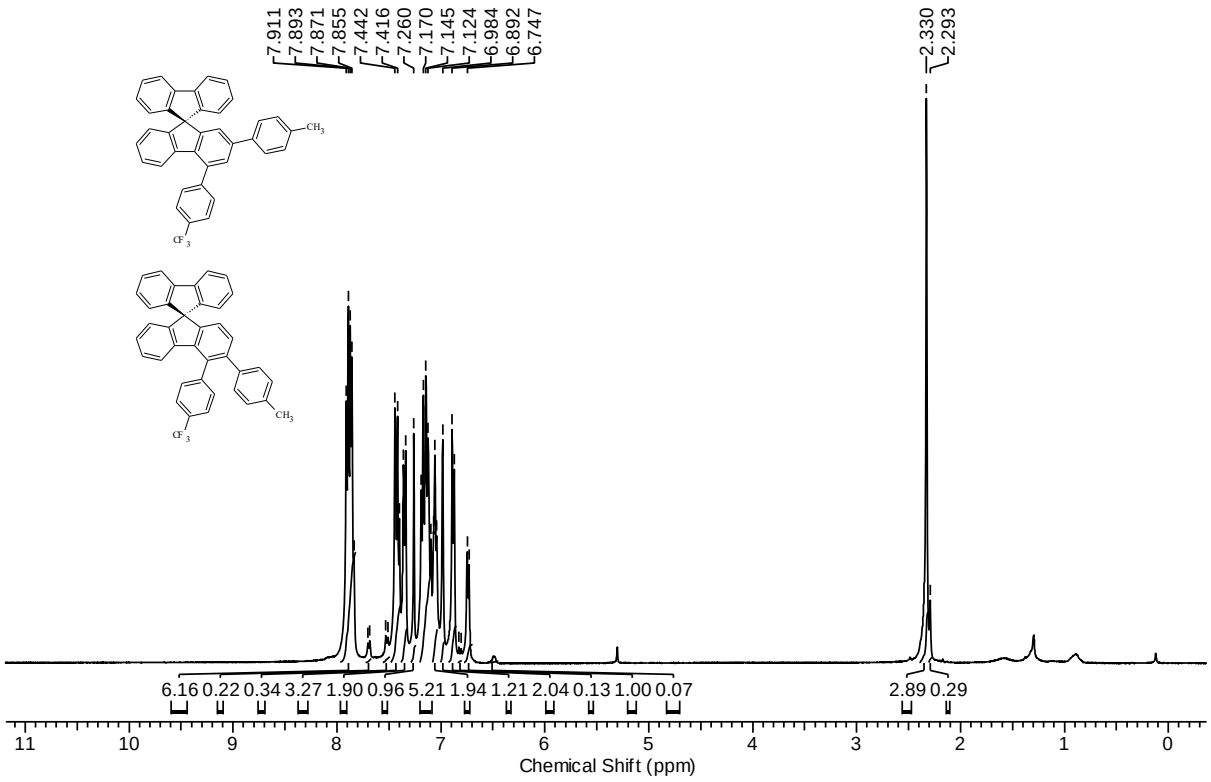


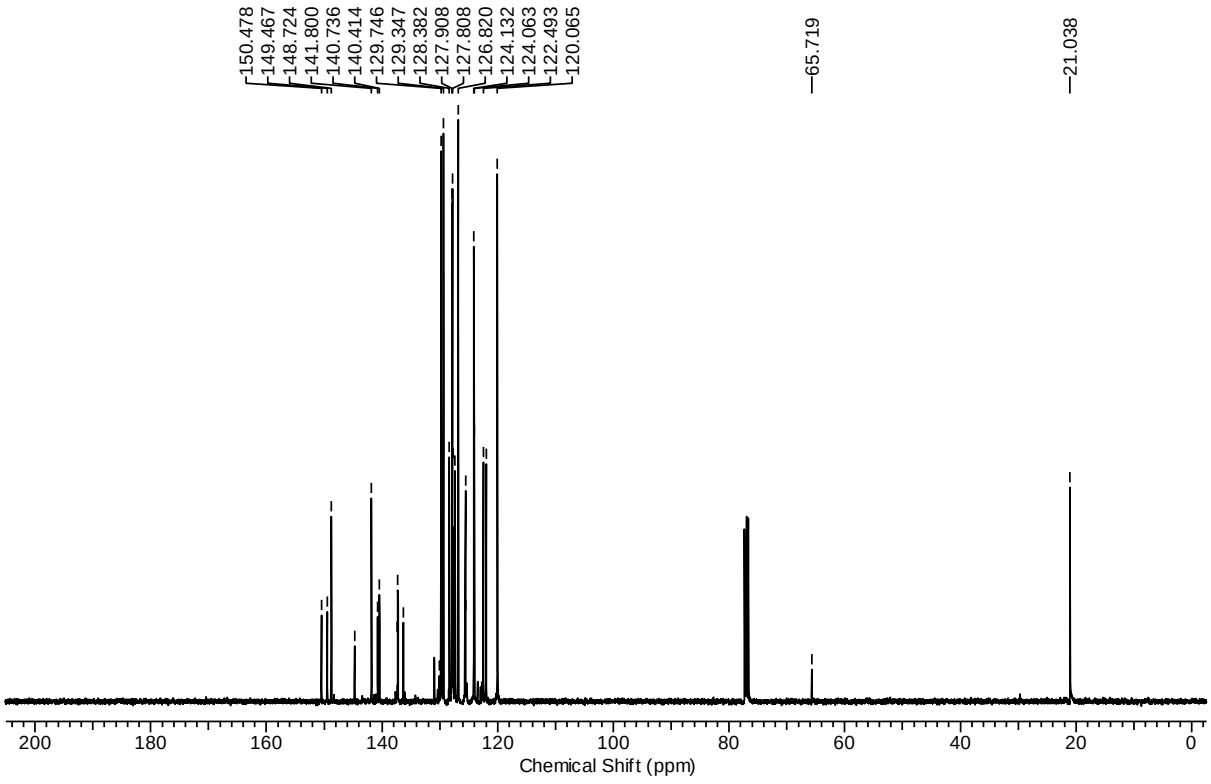
2-([1,1'-Biphenyl]-4-yl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9g)



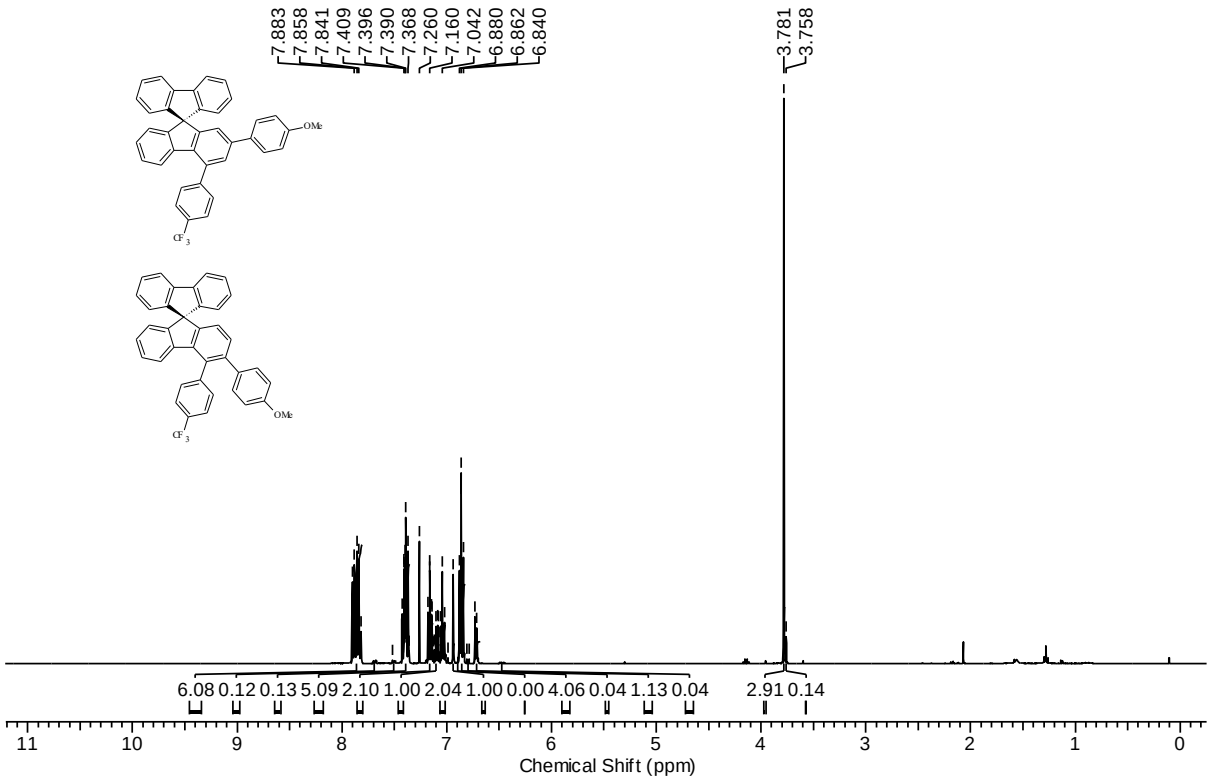


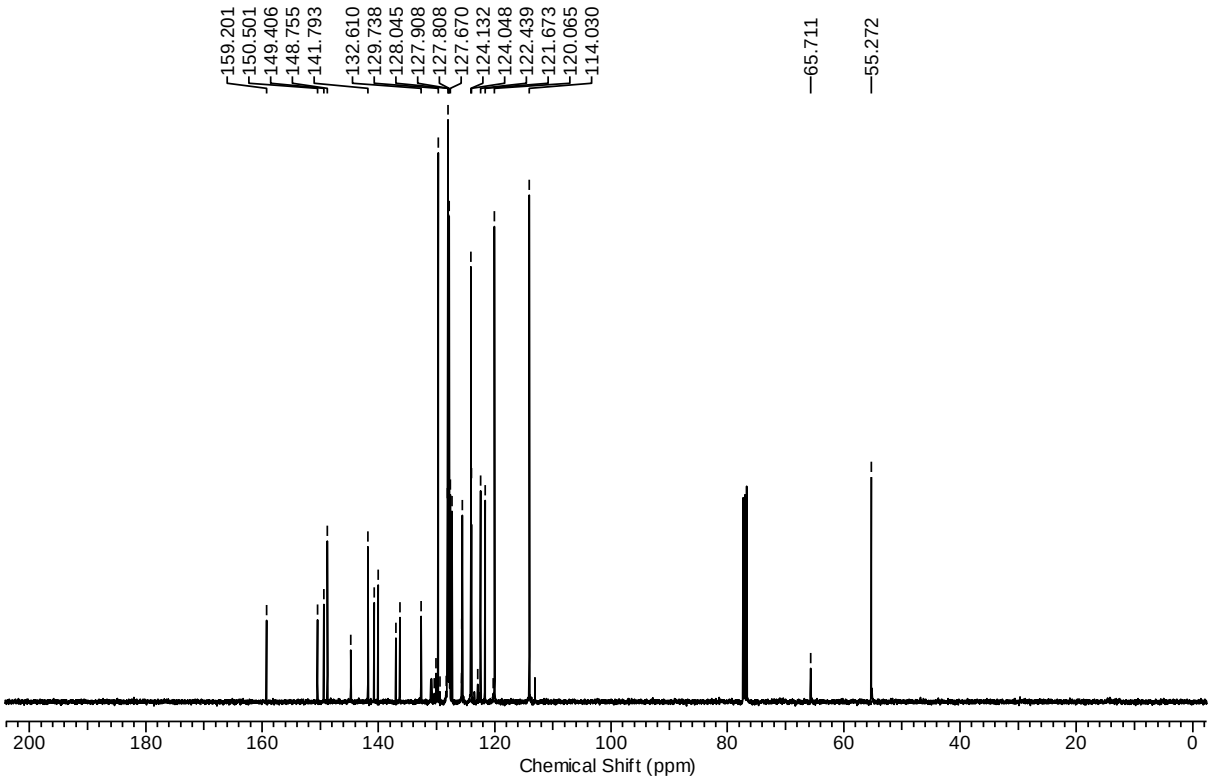
2-(*p*-Tolyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9h)



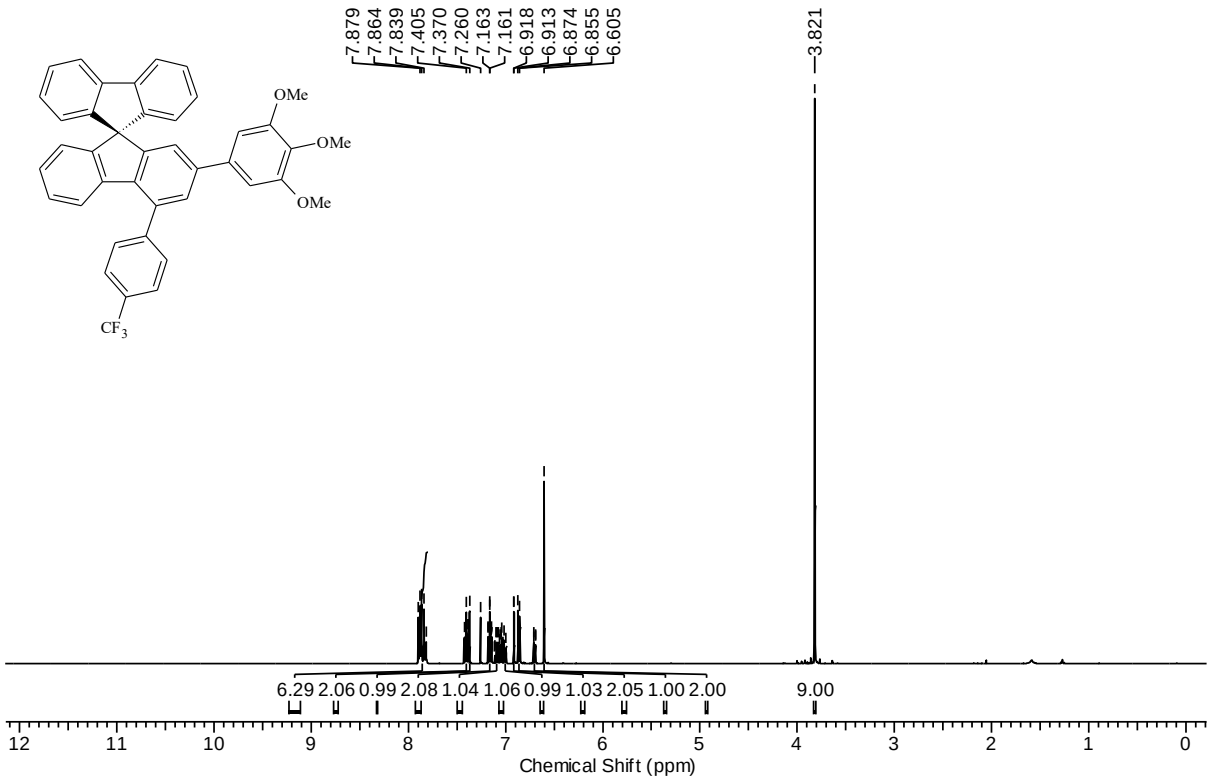


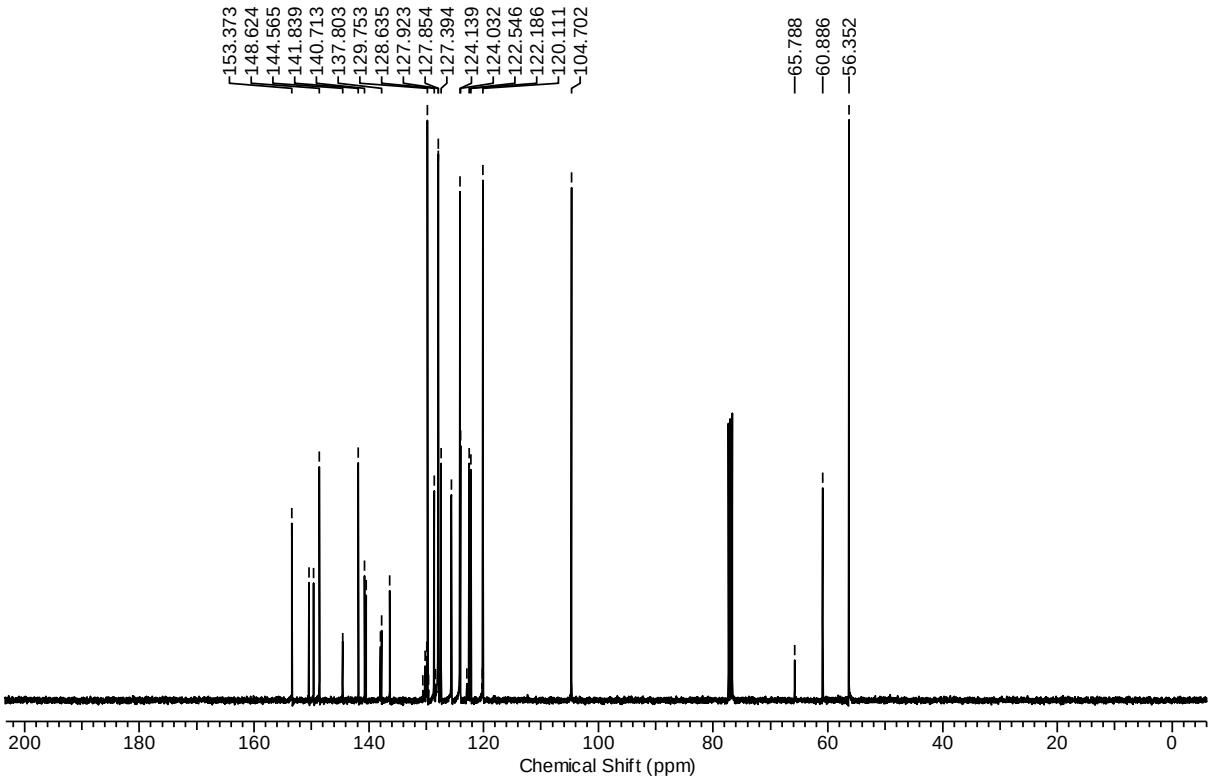
2-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9i)



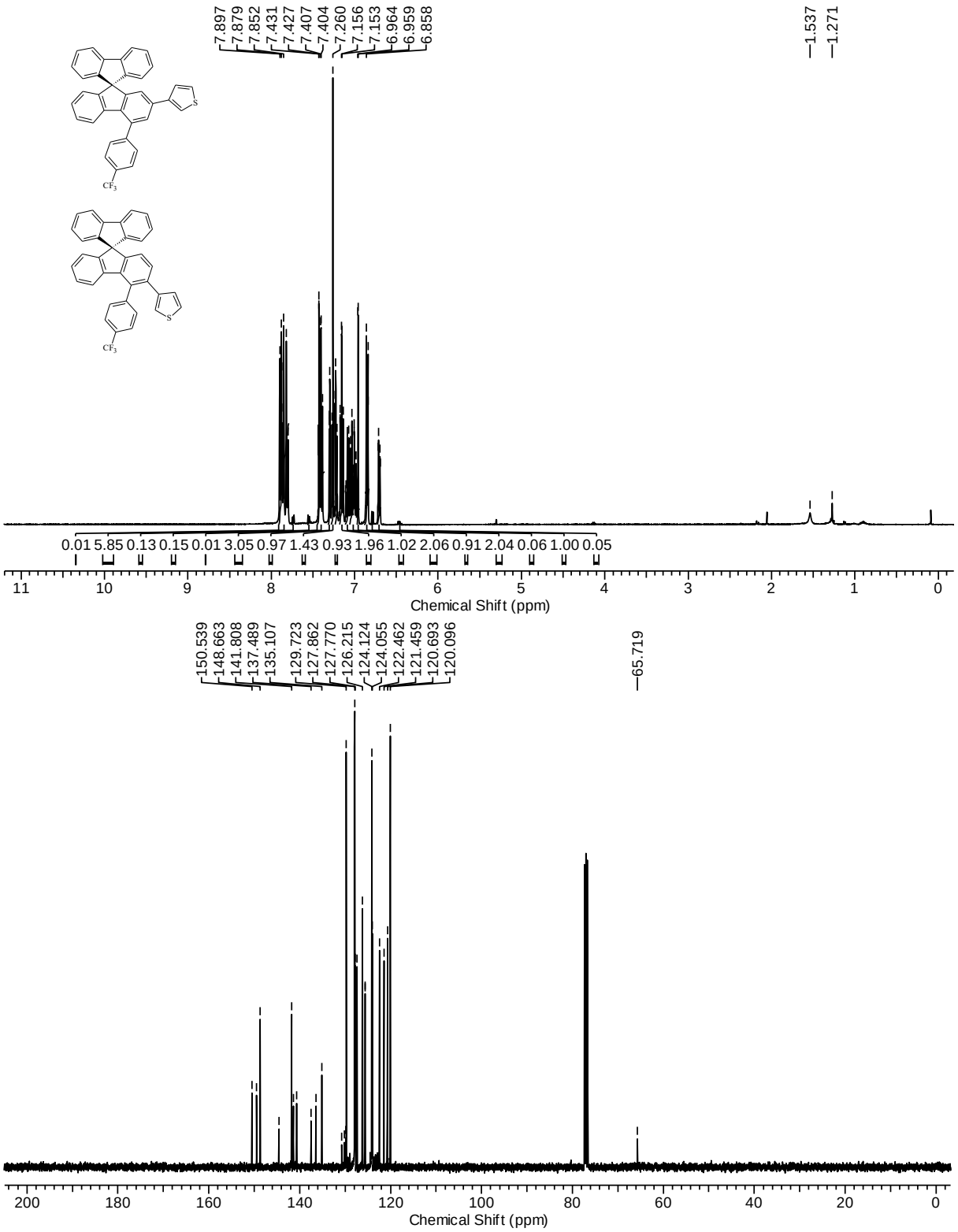


4-(4-(Trifluoromethyl)phenyl)-2-(3,4,5-trimethoxyphenyl)-9,9'-spirobi[fluorene] (9j)

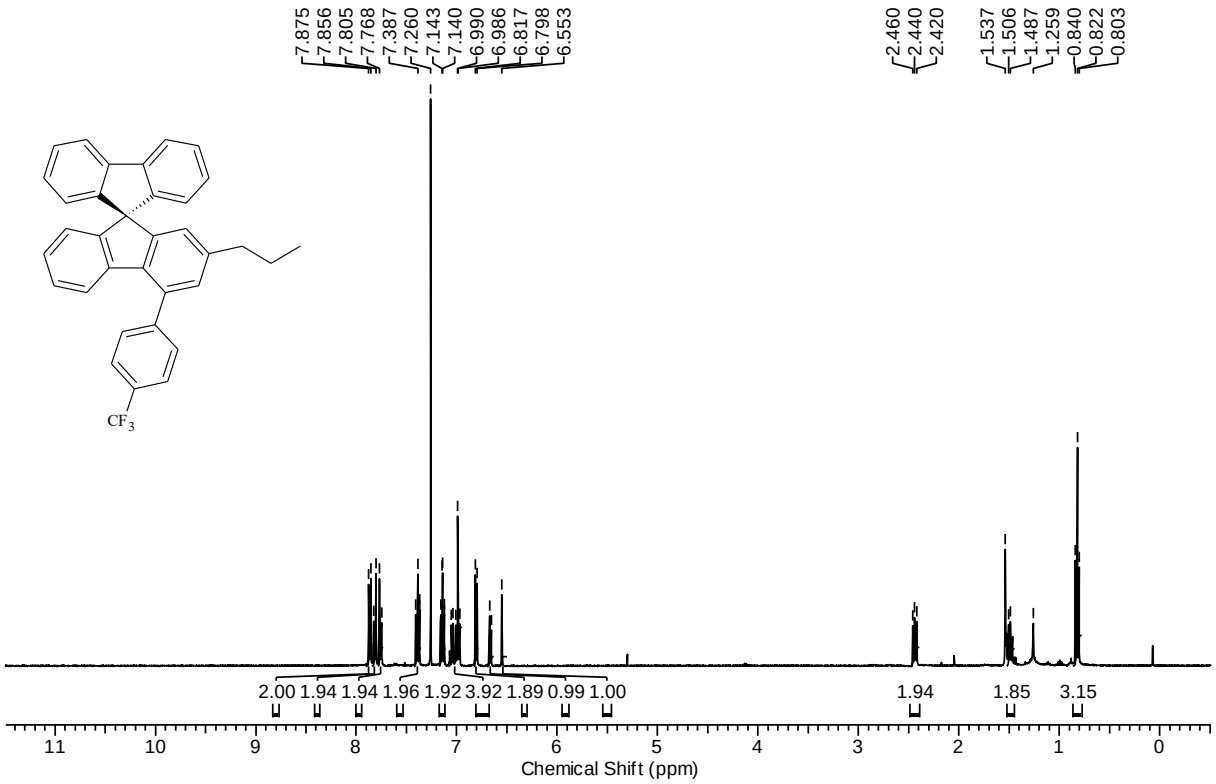


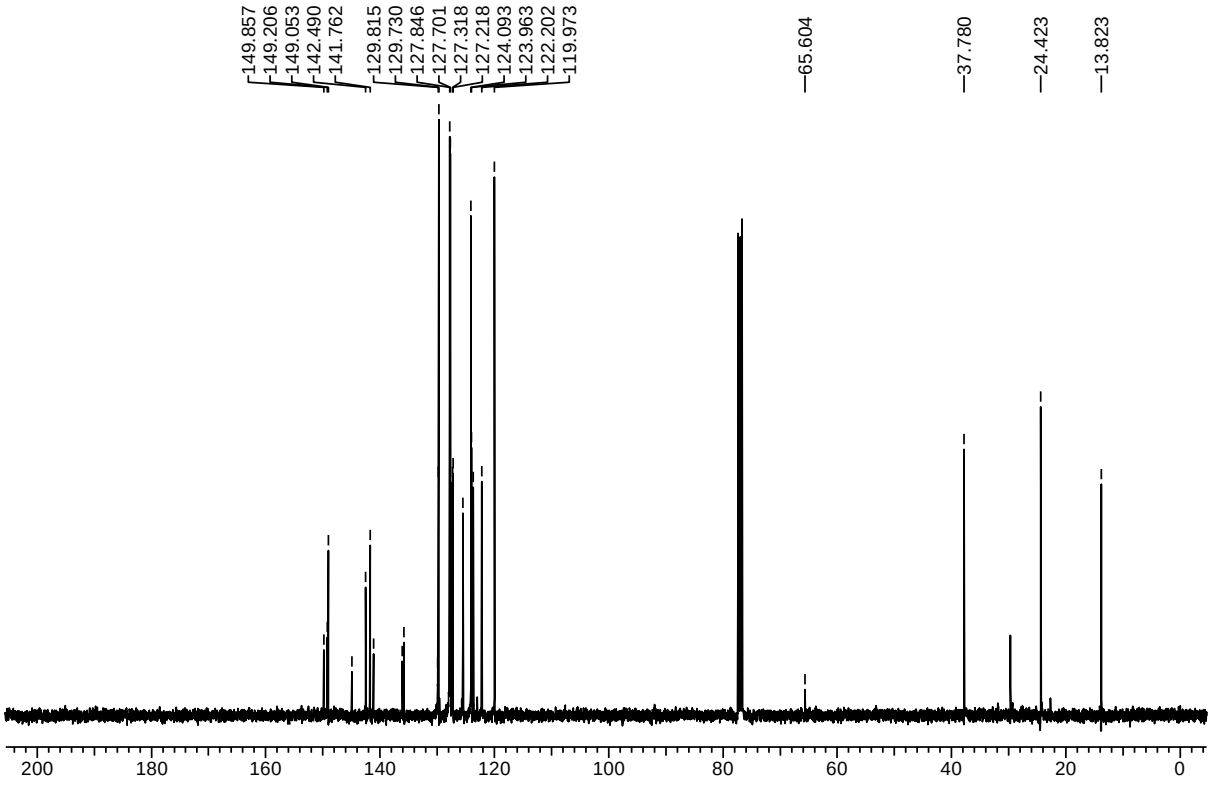


3-(4-(4-(Trifluoromethyl)phenyl)-9,9'-spirobi[fluoren]-2-yl)thiophene (9l)

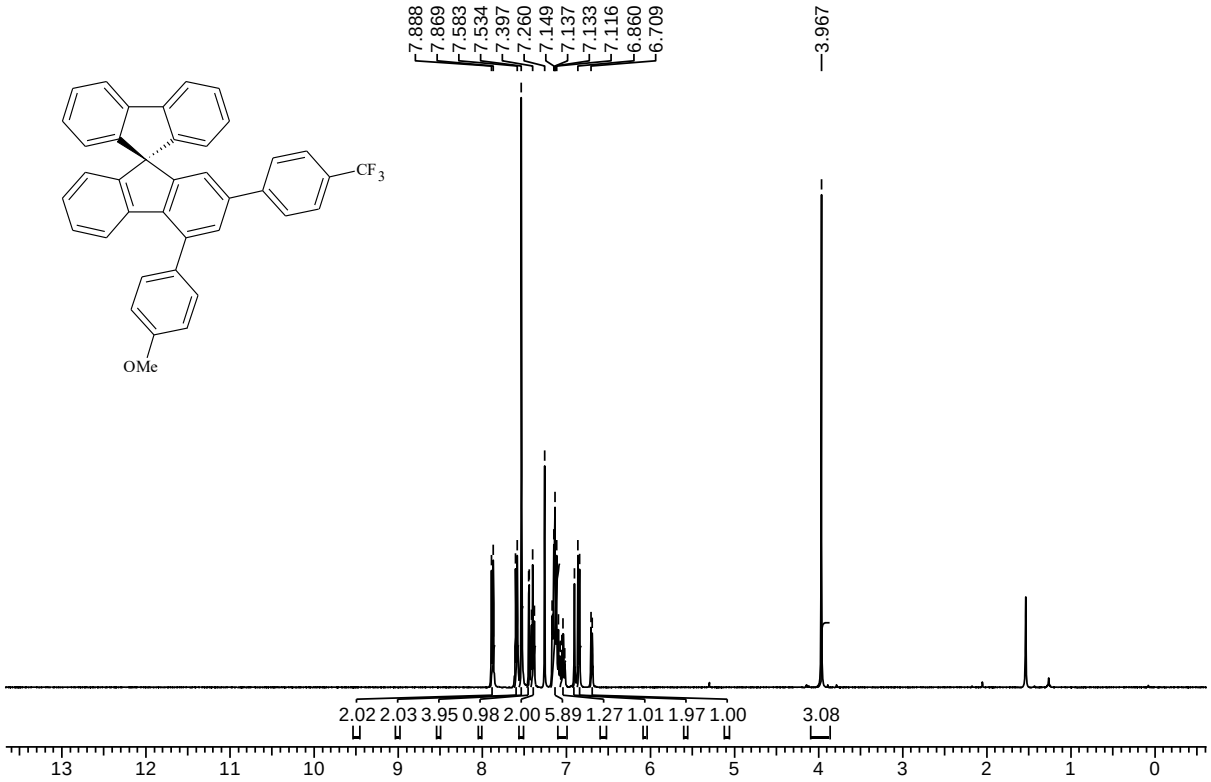


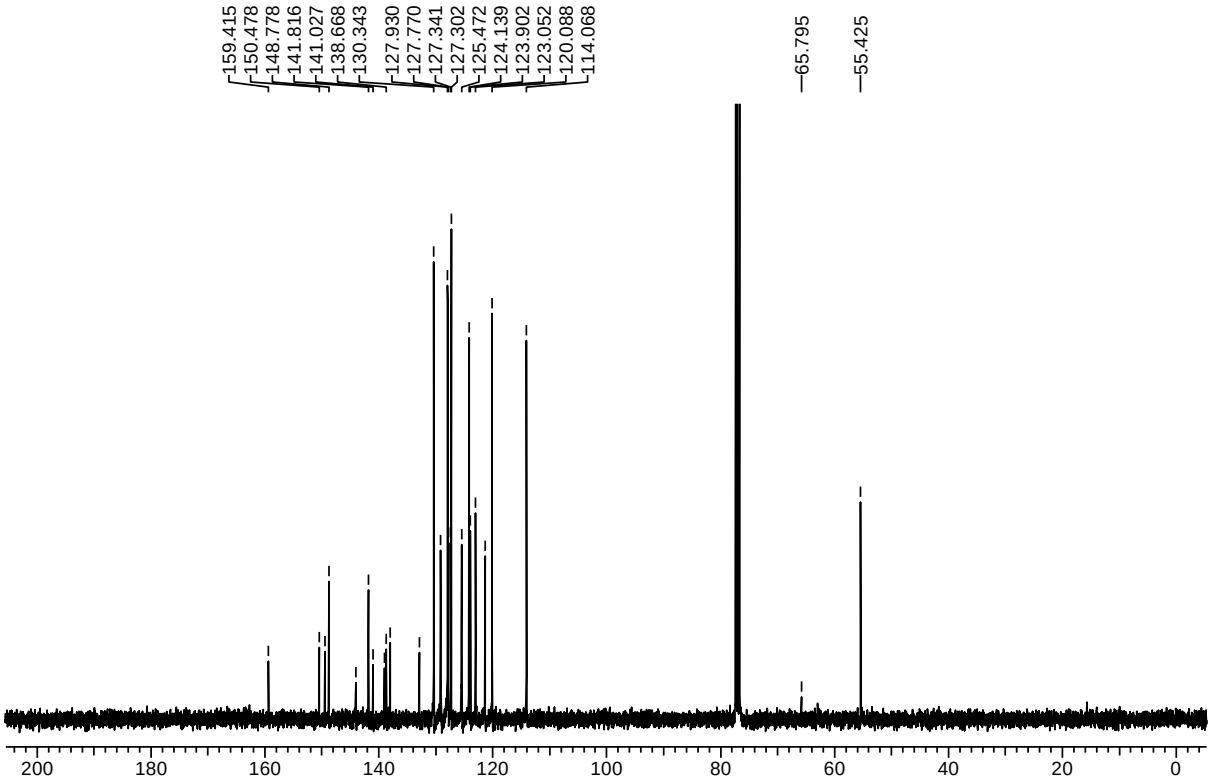
2-Propyl-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9m)





4-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-9,9'-spirobi[fluorene] (9n)





2,4-Bis(4-methoxyphenyl)-9,9'-spirobi[fluorene] (9o)